Table of Contents

I. General Information

II. Synthesis of Starting Materials

III. Control Reactions

IV. Reaction Optimization – Thiol Evaluation

V. Direct Allylic Arylation Reactions

VI. Additional Allylic Arylation Examples

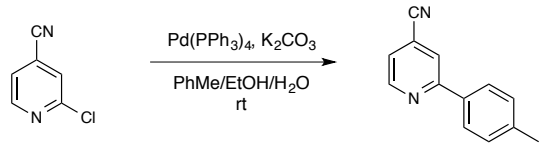
VII. References

VIII. NMR Spectra

I. General Information

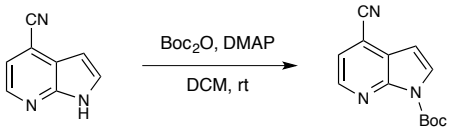
Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] $Ir(ppy)_3$ (sublimed grade) was purchased from Sigma-Aldrich and used as recieved. Reagent grade acetone was used for the direct allylic arylation reactions. All other solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (Fluka, 230–400 mesh), Iatrobeads (6RS-8060) or Florisil according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching or $KMnO_4$ stain. ^1H NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz unless otherwise noted and are internally referenced to residual protio $CDCl_3$ signals (7.26 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz (125 MHz) and data are reported in terms of chemical shift relative to $CDCl_3$ (77.16 ppm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (cm^{-1}). High Resolution Mass Spectra were obtained from the Princeton University Mass Spectral Facility.

II. Synthesis of Starting Materials



2-(*p*-Tolyl)isonicotinonitrile: A solution of 2-chloroisonicotinonitrile (693 mg, 5.00 mmol, 1 equivs.), *p*-tolylboronic acid (1.02 g, 12.5 mmol, 1.50 equivs.) and K_2CO_3 (1.73 g, 12.5 mmol, 1.50 equivs.) in toluene/ethanol/water (4:1:1, 51 mL) was sparged with nitrogen for 20 minutes. To the biphasic solution was added $Pd(PPh_3)_4$ (289 mg, 0.250 mmol, 0.05 equivs.), then the reaction mixture was heated to 110 °C and held for 8 hours. The yellow solution was cooled to rt and poured into water (50 mL). The aqueous phase was extracted with EtOAc (3 × 50 mL), then the combined organic extracts were washed with 1.0 M aqueous NaOH (50 mL) and brine (50 mL), dried ($MgSO_4$), then concentrated *in vacuo* to afford a yellow oil. Purification of the crude product by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) gave the *title compound* (94%, 915 mg, 4.71 mmol) as a colorless crystalline solid; δ_H (500 MHz, $CDCl_3$) 8.83 (d, J = 5.0 Hz, 1H), 7.92 (br s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.41 (dd, J = 5.0, 1.4 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 2.43 (s, 3H); δ_C (125 MHz, $CDCl_3$) 158.9, 150.7, 140.7, 134.7, 130.0, 127.0, 122.9, 121.9, 121.2, 117.0, 21.5.

Data are consistent with those reported in the literature.[4]



***tert*-Butyl 4-cyano-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate:** To a stirred suspension of 1*H*-pyrrolo[2,3-*b*]pyridine-4-carbonitrile (300 mg, 2.10 mmol, 1.0 equivs.) in MeCN (4.2 mL, 0.5 M) at rt were added di-*tert*-butyl dicarbonate (503 mg, 2.31 mmol, 1.1 equivs.) and DMAP (5.1 mg, 0.042 mmol, 0.02 equivs.). The pale brown suspension was stirred at rt for 1 hour during which time the starting material dissolved. The solution was concentrated *in vacuo* to afford a pale brown solid that was purified

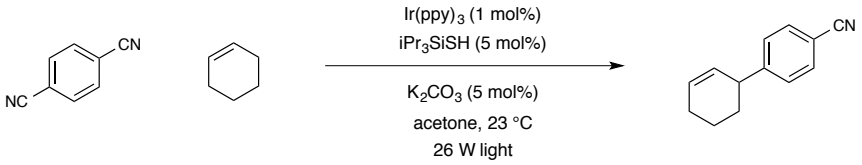
by flash column chromatography (SiO_2, DCM → DCM/EtOAc – 99:1) to afford the *title compound* (91%, 463 mg, 1.90 mmol) as a colorless crystalline solid; IR ν_{max}/cm^{-1} 2984, 2236, 1724, 1523, 1393, 1366, 1312, 1274, 1162, 1132, 821, 731; δ_H (500 MHz, $CDCl_3$) 8.62 (d, J = 5.0 Hz, 1H), 7.87 (d, J = 4.1 Hz, 1H), 7.45 (d, J = 5.0 Hz, 1H), 6.75 (d, J = 4.1 Hz, 1H), 1.69 (s, 9H); δ_C (125 MHz, $CDCl_3$) 148.3, 147.3, 145.1, 129.9, 123.8, 120.6, 115.9, 112.0, 102.9, 85.5, 28.2; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{14}N_3O_2$) requires m/z 244.1081, found m/z 244.1083.

III. Control Reactions

[a] All reactions were run on 0.25 mmol scale for 24 h.

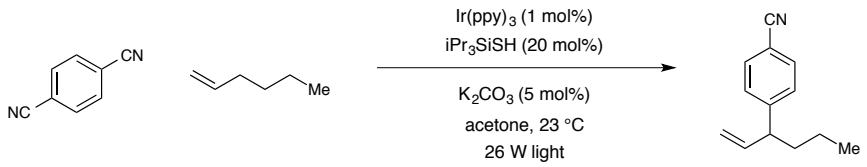
[b] % Yields were calculated by ^{1}H NMR spectroscopy using 1,3-bis(trifluoromethyl)-5-bromobenzene (0.25 mmol) as an internal standard.

Figure 3a. Compound 13.



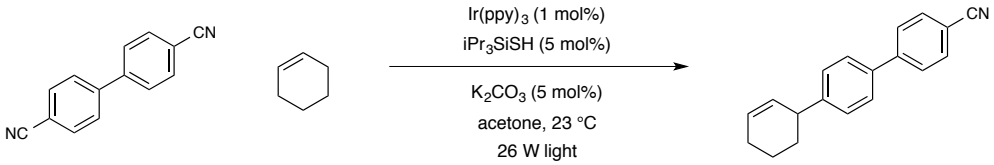
Conditions[a]	Product Yield[b]
Standard	**86%**
No photocatalyst	0%
No thiol	1%
No light	0%
No base	11%

Figure 3a, Compound 19.



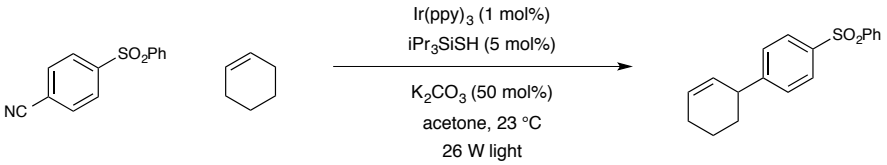
Conditions[a]	Product Yield[b]
Standard	**70%**
No photocatalyst	0%
No thiol	0%
No light	0%
No base	6%

Figure 3b, Compound 32.



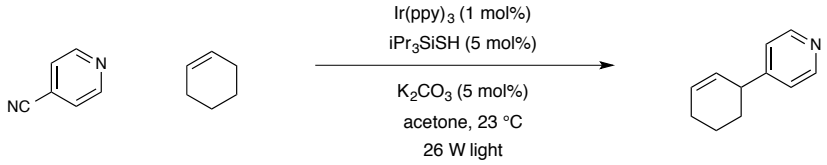
Conditions[a]	Product Yield[b]
Standard	**67%**
No photocatalyst	13%
No thiol	0%
No light	0%
No base	0%

Figure 3b, Compound 33.



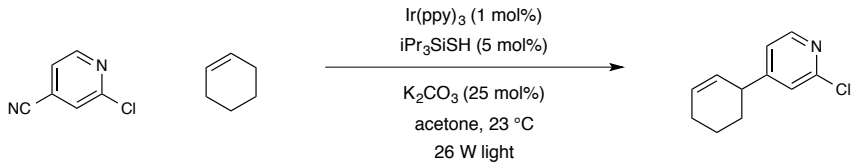
Conditions[a]	Product Yield[b]
Standard	**71%**
No photocatalyst	6%
No thiol	29%
No light	0%
No base	0%

Figure 3b, Compound 34.



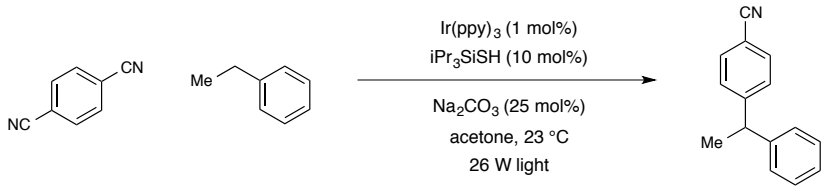
Conditions[a]	Product Yield[b]
Standard	**86%**
No photocatalyst	5%
No thiol	0%
No light	0%
No base	48%

Figure 3b, Compound 35.



Conditions[a]	Product Yield[b]
Standard	**71%**
No photocatalyst	0%
No thiol	0%
No light	0%
No base	4%

Figure 4d. – Ethylbenzene



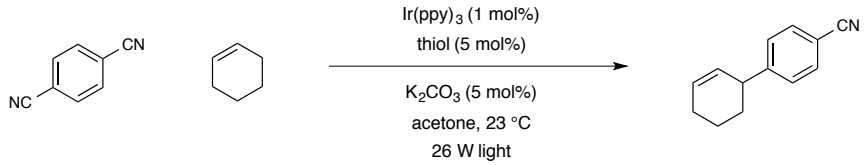
Conditions[a]	Product Yield[b]
Standard	**65%**
No photocatalyst	0%
No thiol	0%
No light	0%
No base	5%

IV. Reaction Optimization – Thiol Evaluation

[a] All reactions were run on 0.25 mmol scale for 24 h.

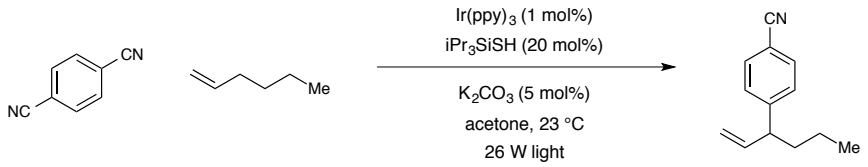
[b] % Yields were calculated by ^{1}H NMR spectroscopy using 1,3-bis(trifluoromethyl)-5-bromobenzene (0.25 mmol) as an internal standard.

Figure 3a. Compound 13.



Thiol	Product Yield[a,b]
Thiophenol	20%
Methyl thioglycolate	75%
2,2,2-Trifluoroethanethiol	94%
Triphenylsilanethiol	93%
Triisopropylsilanethiol	92%

Figure 3a, Compound 19.

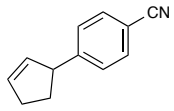


Conditions[a]	**Product Yield**[a,b]
Thiophenol	0%
Methyl thioglycolate	0%
2,2,2-Trifluoroethanethiol	0%
Triphenylsilanethiol	0%
Triisopropylsilanethiol	64%

While a number of thiols were found to be suitable catalysts for reactions employing cyclic alkene substrates, only triisopropylsilane was found to be suitable for terminal alkenes due to competing thiol-ene reactions. Triisopropylsilane thiol was therefore employed as the catalyst in all reactions.

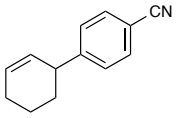
V. Direct Allylic Arylation Reactions

General Procedure for the Allylic Arylation Reaction: To a 12 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding aromatic nitrile (0.75 mmol, 1.0 equiv.), the corresponding alkene (0.75–3.75 mmol, 1.0–5.0 equivs., if solid), K_2CO_3 (0.038–0.375 mmol, 0.05–0.50 equivs.) and *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (7.5 μmol, 0.01 equivs.). The vial was sealed and placed under an atmosphere of nitrogen, then acetone (7.5 mL, 0.1 M), the corresponding alkene (0.75–3.75 mmol, 1.0–5.0 equivs., if liquid) and finally triisopropylsilanethiol (0.038–0.188 mmol, 0.05–0.25 equivs.) were added. The reaction mixture was then cooled to –78 ºC and degassed via vacuum evacuation (5 min.) and subsequent backfill with nitrogen then warming to room temperature (×3). After the third cycle, the reaction was placed in between 2 × 26 W fluorescent lamps (approximately 1 cm from each lamp) and irradiated for the indicated time period (upon complete consumption of the arene, a presistent green/yellow fluorescence was generally observed). The reaction mixture was then concentrated (*Caution: Acetone cyanohydrin generated during the course of the reaction*), then the residue was purified by flash chromatography on silica gel using the indicated solvent system to afford the allylic arylation product.



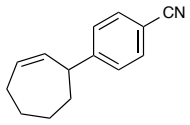
4-(Cyclopent-2-en-1-yl)benzonitrile (Fig. 3a, Compound 12): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclopentene (331 μL, 3.75 mmol, 5 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford the *title compound* (100 mg, 0.591 mmol, 79%) as a colorless oil; δ_H (500 MHz, $CDCl_3$) 7.57 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 6.04–5.97 (m, 1H), 5.76–5.70 (m, 1H), 4.00–3.87 (m, 1H), 2.58–2.37 (m, 3H), 1.75–1.62 (m, 1H); δ_C (125 MHz, $CDCl_3$) 152.3, 133.5, 133.0, 132.4, 128.2, 119.3, 109.9, 51.5, 33.7, 32.6.

Data are consistent with those reported in the literature.[5]

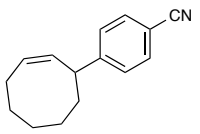


1',2',3',4'-Tetrahydro-[1,1'-biphenyl]-4-carbonitrile (Fig. 3a, Compound 13): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford the *title compound* (120 mg, 0.655 mmol, 87%) as a colorless oil; δ_H (500 MHz, $CDCl_3$) 7.58 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 5.99–5.92 (m, 1H), 5.69–5.62 (m, 1H), 3.51–3.40 (m, 1H), 2.14–2.06 (m, 2H), 2.06–1.97 (m, 1H), 1.77–1.68 (m, 1H), 1.68–1.58 (m, 1H), 1.57–1.47 (m, 1H); δ_C (125 MHz, $CDCl_3$) 152.4, 132.3, 129.8, 128.7, 128.6, 119.3, 109.9, 42.1, 32.5, 25.0, 21.0.

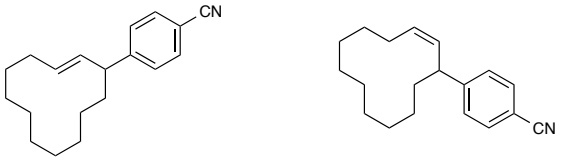
Data are consistent with those reported in the literature.[6]



4-(Cyclohept-2-en-1-yl)benzonitrile (Fig. 3a, Compound 14): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cycloheptene (438 μL, 3.75 mmol, 5 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford the *title compound* (108 mg, 0.547 mmol, 73%) as a colorless oil; IR ν_{max}/cm^{-1} 2921, 2226, 1607, 1503, 1444, 829, 818, 685; δ_H (500 MHz, $CDCl_3$) 7.59 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 5.96–5.85 (m, 1H), 5.70–5.61 (m, 1H), 3.63–3.54 (m, 1H), 2.31–2.15 (m, 2H), 1.98–1.88 (m, 1H), 1.85–1.62 (m, 4H), 1.52–1.40 (m, 1H); δ_C (125 MHz, $CDCl_3$) 153.3, 135.2, 133.1, 132.5, 128.3, 119.3, 109.9, 47.3, 36.0, 30.1, 28.9, 26.9; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{16}N$) requires m/z 198.1277, found m/z 198.1275.



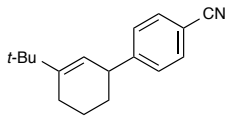
(*Z*)-4-(Cyclooct-2-en-1-yl)benzonitrile (Fig. 3a, Compound 15): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclooctene (488 μL, 3.75 mmol, 5 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford the *title compound* (136 mg, 0.644 mmol, 86%) as a colorless oil; IR ν_{max}/cm^{-1} 2923, 2226, 1607, 1503, 1448, 823, 763, 708; δ_H (500 MHz, $CDCl_3$) 7.59 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.80–5.72 (m, 1H), 5.55–5.48 (m, 1H), 3.84–3.76 (m, 1H), 2.40–2.28 (m, 1H), 2.21–2.11 (m, 1H), 1.89–1.33 (m, 8H); δ_C (125 MHz, $CDCl_3$) 152.2, 132.5, 132.4, 130.5, 128.3, 119.3, 109.9, 42.7, 37.3, 29.6, 26.8, 26.7, 26.0; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{18}N$) requires m/z 212.1434, found m/z 212.1436.



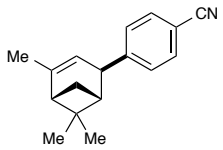
Major **Minor**

(*E*)-4-(Cyclododec-2-en-1-yl)benzonitrile and (*Z*)-4-(cyclododec-2-en-1-yl)benzonitrile (Fig. 3a, Compound 16): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), (*E*)-cyclododecene (723 μL, 3.75 mmol, 5 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford an inseparable mixture of the *title compounds* (143 mg, 0.535 mmol, 71%, 2.2:1.0 *E*:*Z*) as a colorless oil; IR ν_{max}/cm^{-1} 2924, 2854, 2227, 1607, 1503, 1463, 1445, 975, 826; δ_H (500 MHz, $CDCl_3$) 7.57 (d, *J* = 8.2 Hz, $2H_{Minor}$), 7.57 (d, *J* = 8.2 Hz, $2H_{Major}$), 7.33 (d, *J* = 8.2 Hz,

2H$_{Minor}$), 7.31 (d, J = 8.0 Hz, 2H$_{Major}$), 5.57 (ddd, J = 14.8, 10.3, 4.3 Hz, 1H$_{Major}$), 5.48–5.36 (m, 3H), 3.86 (td, J = 9.2, 5.5 Hz, 1H$_{Minor}$), 3.28 (ddd, J = 12.7, 9.9, 3.6, 1H$_{Major}$), 2.59–2.48 (m, 1H$_{Minor}$), 2.25–2.16 (m, 1H$_{Major}$), 2.01–1.85 (m, 2H), 1.83–1.72 (m, 2H), 1.69–1.16 (m, 30H); δ_C (125 MHz, $CDCl_3$) 152.0, 151.8, 133.4, 132.7, 132.4, 132.4, 132.2, 131.2, 128.2, 128.0, 119.3, 119.3, 109.8, 109.7, 49.7, 40.4, 34.6, 34.4, 32.4, 26.9, 26.3, 26.2, 25.4, 25.0, 24.9, 24.8, 24.8, 24.6, 24.5, 24.4, 24.4, 23.9, 22.5, 22.2; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{26}N$) requires m/z 268.2060, found m/z 268.2058.

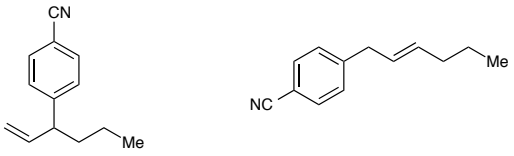


5'-(*tert*-Butyl)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (Fig. 3a, Compound 17): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), 1-(*tert*-butyl)cyclohex-1-ene (625 μL, 3.75 mmol, 5 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford an inseparable mixture of the *title compound* and a minor uncharacterized isomeric product (Combined yield: 166 mg, 0.694 mmol, 92%, >20:1) as a colorless oil; IR ν_{max}/cm^{-1} 2932, 2865, 2227, 1607, 1501, 1361, 838, 827; δ_H (500 MHz, $CDCl_3$) 7.57 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.45–5.42 (m, 1H), 3.49–3.42 (m, 1H), 2.17–2.03 (m, 2H), 2.01–1.92 (m, 1H), 1.79–1.69 (m, 1H), 1.63–1.52 (m, 1H), 1.40 (dddd, J = 13.1, 10.8, 8.3, 2.8 Hz, 1H), 1.08 (s, 9H); δ_C (125 MHz, $CDCl_3$) 153.5, 148.6, 132.3, 128.7, 119.4, 119.3, 109.7, 42.5, 35.7, 32.4, 29.3, 24.5, 21.9; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{22}N$) requires m/z 240.1747, found m/z 240.1745.



4-((1*R*,2*R*,5*S*)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-yl)benzonitrile (Fig. 3a, Compound 18): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), α-pinene (595 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford an inseparable mixture of the *title compound* and minor uncharacterized isomeric products (Combined yield: 159 mg, 0.670 mmol, 89%, >10:1) as a colorless oil; IR ν_{max}/cm^{-1} 2920, 2228, 1609, 1502, 1366, 1251, 1021, 857, 823; δ_H (500 MHz, $CDCl_3$) 7.57 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.31 (dd, *J* = 3.0, 1.5 Hz, 1H), 3.65–3.62 (m, 1H), 2.13–2.04 (m, 3H), 1.80–1.78 (m, 3H), 1.33 (s, 3H), 1.22–1.17 (m, 1H), 1.00 (s, 3H); δ_C (125 MHz, $CDCl_3$) 151.1, 147.5, 132.1, 129.4, 119.4, 116.8, 109.7, 48.2, 46.9, 45.8, 42.3, 26.5, 26.2, 23.3, 20.7; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{20}N$) requires m/z 238.1590, found m/z 238.1590.

Data are consistent with those reported in the literature.[7]



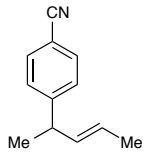
Major **Minor**

4-(Hex-1-en-3-yl)benzonitrile and (*E*)-4-(hex-2-en-1-yl)benzonitrile (Fig. 3a, Compound 19): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), 1-hexene (465 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (32.2 μL, 0.150 mmol, 0.20 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was

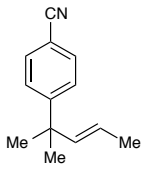
concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford an inseparable mixture of the *title compounds* and minor uncharacterized isomeric products (Combined yield: 88 mg, 0.475 mmol, 63%, 1.4:1.0) as a colorless oil; IR ν_{max}/cm^{-1} 2959, 2930, 2872, 2228, 1607, 1504, 969, 917, 837, 817; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}N$) requires m/z 186.1277, found m/z 186.1278.

4-(Hex-1-en-3-yl)benzonitrile: δ_H (500 MHz, $CDCl_3$) 7.59 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 5.89 (ddd, *J* = 17.5, 10.3, 7.6 Hz, 1H), 5.07 (dt, *J* = 10.3, 1.4 Hz, 1H), 5.03 (dt, *J* = 17.5, 1.4 Hz, 1H), 3.31 (dt, *J* = 7.6, 7.5 Hz, 1H), 1.76–1.61 (m, 2H), 1.36–1.15 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 150.4, 141.0, 132.4, 128.6, 119.2, 115.3, 110.1, 49.8, 37.4, 20.7, 14.0.

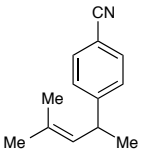
(*E*)-4-(Hex-2-en-1-yl)benzonitrile: δ_H (500 MHz, $CDCl_3$) 7.57 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.54–5.50 (m, 2H), 3.38 (d, *J* = 4.9 Hz, 2H), 2.04–1.98 (m, 2H), 1.44–1.36 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 146.9, 133.6, 132.3, 129.4, 127.3, 119.3, 109.9, 39.2, 34.7, 22.6, 13.8.



(*E*)-4-(Pent-3-en-2-yl)benzonitrile (Fig. 3a, Compound 20): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), (*E*)-2-pentene (405 μL, 3.75 mmol, 5 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford an inseparable mixture of the *title compound* and minor uncharacterized isomeric products (Combined yield: 109 mg, 0.637 mmol, 85%, 4.9:1.0) as a colorless oil; IR ν_{max}/cm^{-1} 2968, 2228, 1607, 1503, 1452, 1015, 967, 837; δ_H (500 MHz, $CDCl_3$) 7.58 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.55 (ddq, *J* = 15.3, 6.4, 1.3 Hz, 1H), 5.51–5.45 (m, 1H), 3.50–3.42 (m, 1H), 1.68 (d, *J* = 6.0 Hz, 3H), 1.33 (d, *J* = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 152.2, 134.7, 132.4, 128.1, 125.3, 119.3, 109.9, 42.6, 21.2, 18.1; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}N$) requires m/z 172.1121, found m/z 172.1122.



Major

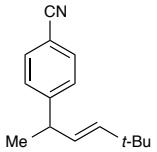


Minor

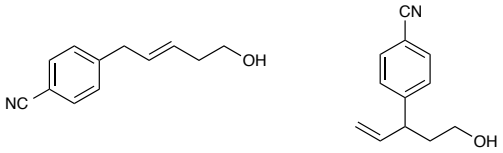
(*E*)-4-(2-Methylpent-3-en-2-yl)benzonitrile and 4-(4-methylpent-3-en-2-yl)benzonitrile (Fig. 3a, Compound 21): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), 2-methyl-2-pentene (457 μL, 3.75 mmol, 5 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford an inseparable mixture of the *title compounds* (Combined yield: 125 mg, 0.675 mmol, 90%, 1.4:1.0) as a colorless oil; IR ν_{max}/cm^{-1} 2968, 2228, 1606, 1503, 1450, 972, 835; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}N$) requires m/z 186.1277, found m/z 186.1277.

(*E*)-4-(2-Methylpent-3-en-2-yl)benzonitrile: δ_H (500 MHz, $CDCl_3$) 7.57 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.58 (dq, *J* = 15.5, 1.5 Hz, 1H), 5.47 (dq, *J* = 15.5, 6.3 Hz, 1H), 1.71 (dd, *J* = 6.3, 1.5 Hz, 3H), 1.38 (s, 6H); δ_C (125 MHz, $CDCl_3$) 155.2, 139.8, 132.0, 127.2, 122.6, 119.3, 109.6, 41.0, 28.8, 18.1.

4-(4-Methylpent-3-en-2-yl)benzonitrile: δ_H (500 MHz, $CDCl_3$) 7.57 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.21 (dqq, *J* = 9.1, 1.7, 1.3 Hz, 1H), 3.69 (dq, *J* = 9.1, 7.0 Hz, 1H), 1.71 (d, *J* = 1.7 Hz, 3H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.30 (d, *J* = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 153.0, 132.4, 128.7, 127.9, 119.3, 109.6, 38.5, 25.9, 22.3, 18.2 (fully substituted alkene carbon not observed).



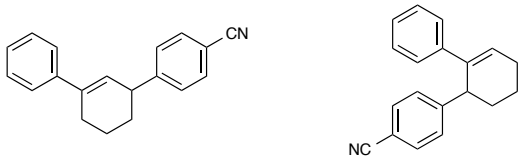
(*E*)-4-(5,5-Dimethylhex-3-en-2-yl)benzonitrile (Fig. 3a, Compound 22) : Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), (*E*)-2,2-dimethyl-3-hexene (601 μL, 3.75 mmol, 5.0 equivs.), triisopropylsilanethiol (16.1 μL, 0.075 mmol, 0.10 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford the *title compound* (129 mg, 0.605 mmol, 81%) as a colorless oil; IR ν_{max}/cm^{-1} 2959, 2867, 2228, 1067, 1504, 1363, 1011, 974, 831; δ_H (500 MHz, $CDCl_3$) 7.58 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.52 (dd, *J* = 15.8, 1.1 Hz, 1H), 5.42 (dd, *J* = 15.8, 6.6 Hz, 1H), 3.45 (qd, *J* = 7.0, 6.6 Hz, 1H), 1.33 (d, *J* = 7.0, 3H), 1.00 (s, 9H); δ_C (125 MHz, $CDCl_3$) 152.5, 141.8, 132.4, 128.1, 128.1, 119.3, 109.8, 42.4, 33.0, 29.8, 21.5; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{20}N$) requires m/z 214.1590, found m/z 214.1590.



Major **Minor**

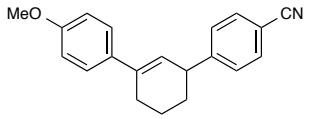
(*E*)-4-(5-Hydroxypent-2-en-1-yl)benzonitrile and 4-(5-hydroxypent-1-en-3-yl)benzonitrile (Fig. 3a, Compound 23): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), 4-penten-1-ol (387 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (40.0 μL, 0.188 mmol, 0.25 equivs.) and acetone (7.5 mL). After 6 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford an inseparable mixture of the *title compounds* and minor uncharacterized isomeric products (Combined yield: 93 mg, 0.497 mmol, 66%, 1.1:1.0) as a colorless oil;

IR ν_{max}/cm^{-1} 3391 (br), 2930, 2228, 1606, 1504, 1414, 1045, 1020, 970, 819; δ_H (500 MHz, $CDCl_3$) 7.60 (d, *J* = 8.3 Hz, $2H_{Minor}$), 7.58 (d, *J* = 8.2 Hz, $2H_{Major}$), 7.33 (d, *J* = 8.3 Hz, $2H_{Minor}$), 7.29 (d, *J* = 8.2 Hz, $2H_{Major}$), 5.92 (ddd, *J* = 17.5, 10.3, 7.6 Hz, $1H_{Minor}$), 5.71–5.63 (m, $1H_{Major}$), 5.58–5.50 (m, $1H_{Major}$), 5.13 (d, *J* = 10.3 Hz, $1H_{Minor}$), 5.11 (d, *J* = 17.5 Hz, $1H_{Minor}$), 3.71–3.64 (m, $1H_{Minor}$), 3.68 (t, *J* = 6.5 Hz, $2H_{Major}$), 3.61–3.55 (m, $2H_{Minor}$), 3.42 (d, *J* = 6.6 Hz, $2H_{Major}$), 2.07–1.96 (m, $1H_{Minor}$), 2.32 (dt, *J* = 6.5, 6.5 Hz, $2H_{Major}$), 1.99–1.88 (m, $1H_{Minor}$); δ_C (125 MHz, $CDCl_3$) 149.5, 146.3, 140.3, 132.6, 132.4, 130.6, 129.4, 129.3, 128.6, 119.2, 119.1, 116.0, 110.4, 110.1, 62.1, 60.5, 46.2, 39.3, 37.7, 36.0; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}NO$) requires m/z 188.1070, found m/z 188.1068.



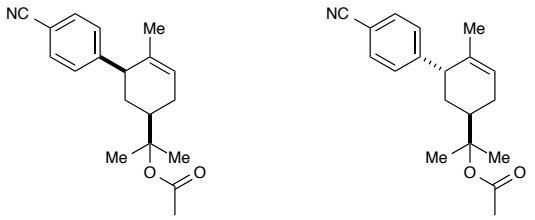
Major **Minor**

1',4',5',6'-Tetrahydro-[1,1':3',1''-terphenyl]-4-carbonitrile and 1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-4-carbonitrile (Fig. 3a, Compound 24). Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), 1-phenyl-cyclohex-1-ene (706 mg, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (16.1 μL, 0.075 mmol, 0.10 equivs.) and acetone (7.5 mL). After 24 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford an inseparable mixture of the *title compounds* and minor uncharacterized isomeric products (Combined yield: 148 mg, 0.571 mmol, 76%, 2.1:1.0) as a colorless oil; IR ν_{max}/cm^{-1} 2930, 2859, 2226, 1606, 1497, 1445, 834, 756, 695; δ_H (500 MHz, $CDCl_3$) 7.60 (d, *J* = 8.3 Hz, $2H_{Major}$), 7.50 (d, *J* = 8.3 Hz, $2H_{Minor}$), 7.44 (d, *J* = 7.4 Hz, $2H_{Major}$), 7.38–7.09 (m, 12H), 6.43 (t, *J* = 4.0 Hz, $1H_{Minor}$), 6.08–6.06 (m, $1H_{Major}$), 4.11–4.06 (m, $1H_{Minor}$), 3.69–3.61 (m, $1H_{Major}$), 2.60–2.47 (m, $2H_{Major}$), 2.41–2.26 (m, $2H_{Major}$), 2.18–2.06 (m, 2H), 1.98–1.88 (m, $1H_{Major}$), 1.85–1.74 (m, 2H), 1.70–1.45 (m, 3H); δ_C (125 MHz, $CDCl_3$) 152.4, 151.2, 141.9, 141.2, 139.2, 136.9, 132.4, 132.2, 129.4, 129.0, 128.8, 128.5, 128.4, 127.4, 126.9, 125.8, 125.8, 125.3, 119.3, 119.3, 110.1, 109.8, 42.9, 42.9, 32.6, 32.1, 27.4, 26.1, 21.7, 17.7; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}N$) requires m/z 260.1434, found m/z 260.1433.



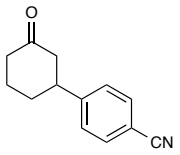
4''-Methoxy-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-4-carbonitrile (Fig. 3a, Compound 25). Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), 4'-methoxy-2,3,4,5-tetrahydro-1-1'-biphenyl[8] (706 mg, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 19:1) to afford an inseparable mixture of the *title compound* and a minor uncharacterized isomeric product (Combined yield: 206 mg, 0.712 mmol, 95%, >19:1) as a colorless oil; δ_H (500 MHz, $CDCl_3$) 7.59 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.00–5.97 (m, 1H), 3.82 (s, 3H), 3.67–3.59 (m, 1H), 2.55–2.44 (m, 2H), 2.13–2.03 (m, 1H), 1.97–1.86 (m, 1H), 1.83–1.73 (m, 1H), 1.60–1.50 (m, 1H); δ_C (125 MHz, $CDCl_3$) 159.1, 152.6, 138.5, 134.4, 132.4, 128.8, 126.3, 124.3, 119.3, 113.8, 110.0, 55.5, 42.9, 32.1, 27.5, 21.7.

Data are consistent with those reported the literature.[6]



(±)-2-((1*R*,3*R*)-4'-Cyano-6-methyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-3-yl)propan-2-yl acetate and (±)-2-((1*S*,3*R*)-4'-cyano-6-methyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-3-yl)propan-2-yl acetate (Fig. 3a, Compound 26). Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), (±)-2-(4-methyl-3-cyclohexenyl)isopropyl acetate (772 mg, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by

flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1) to afford an inseparable mixture of the *title compounds* and minor uncharacterized isomeric products (Combined yield: 188 mg, 0.632 mmol, 84%, ~1.0:1.0) as a colourless oil; IR ν_{max}/cm^{-1} 2934, 2228, 1725, 1367, 1254, 1131, 1017, 838; δ_H (500 MHz, $CDCl_3$) 7.63–7.56 (m, 4H), 7.31–7.25 (m, 4H), 5.79–5.73 (m, 1H), 5.70–5.63 (m, 1H), 3.43–3.39 (m, 1H), 3.39–3.33. (m, 1H), 2.34–2.24 (m, 1H), 2.16–1.77 (m, 13H), 1.73–1.67 (m, 1H), 1.58 (br s, 3H), 1.42 (s, 3H), 1.41 (s, 3H), 1.39–1.35 (br s, 3H), 1.36–1.31 (m, 1H), 1.31 (s, 3H), 1.29 (s, 3H); δ_C (125 MHz, $CDCl_3$) 170.6, 170.3, 134.0, 132.8, 132.5, 132.2, 129.3, 129.1, 125.2, 124.9, 119.3, 119.2, 110.2, 110.1, 84.4, 84.0, 48.7, 46.0, 42.8, 36.6, 35.4, 32.5, 26.9, 26.6, 23.5, 23.4, 23.2, 23.2, 22.6, 22.6, 22.4, 21.6; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{19}H_{23}NNaO_2$) requires m/z 320.1621, found m/z 320.1622.



4-(3-Oxocyclohexyl)benzonitrile (Fig. 3a, Compound 27): Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), 1-(trimethylsiloxy)cyclohexene (219 μL, 1.13 mmol, 1.50 equivs.), triisopropylsilanethiol (8.05 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 3 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 2:1 → 1:1) to afford the *title compound* (124 mg, 0.622 mmol, 83%) as a pale yellow oil; δ_H (500 MHz, $CDCl_3$) 7.63 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 3.08 (dddd, J = 11.7, 11.7, 3.9, 3.9 Hz, 1H), 2.59 (ddt, J = 14.0, 4.2, 2.0 Hz, 1H) 2.54–2.46 (m, 2H), 2.43–2.35 (m, 1H), 2.20–2.13 (m, 1H), 2.13–2.05 (m, 1H), 1.90–1.75 (m, 2H); δ_C (125 MHz, $CDCl_3$) 210.0, 149.6, 132.7, 127.6, 118.9, 110.8, 48.3, 44.8, 41.2, 32.4, 25.4.

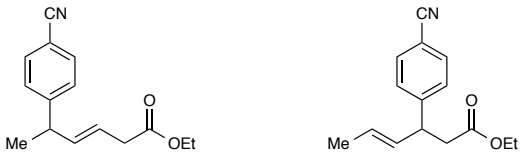
Data are consistent with those reported in the literature.[9]

Alternative procedure:

4-(3-Oxocyclohexyl)benzonitrile (Fig. 3a, Compound 27). Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), 2-cyclohexen-

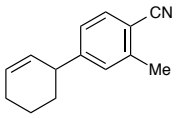
1-ol (368 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.05 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 2:1 → 1:1) to afford the *title compound* (92 mg, 0.462 mmol, 62%) as a pale yellow oil.

Data are consistent with those reported in the literature.[9]

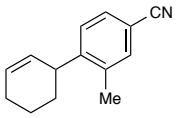


Major **Minor**

Ethyl (*E*)-5-(4-cyanophenyl)hex-3-enoate and ethyl (*E*)-3-(4-cyanophenyl)hex-4-enoate (Fig. 3a, Compound 28). Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), (*E*)-ethyl hex-3-enoate (595 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (16.1 μL, 0.038 mmol, 0.10 equivs.) and acetone (7.5 mL). After 6 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 9:1) to afford an inseparable mixture of the *title compounds* and minor uncharacterized isomeric products (Combined yield: 148 mg, 0.608 mmol, 81%, 1.2:1.0) as a pale yellow oil; IR ν_{max}/cm^{-1} 2975, 2228, 1730, 1251, 1160, 839; δ_H (500 MHz, $CDCl_3$) 7.59 (d, J = 8.5 Hz, $2H_{Minor}$), 7.58 (d, J = 8.5 Hz, $2H_{Major}$), 7.32 (d, J = 8.5 Hz, $2H_{Minor}$), 7.31 (d, J = 8.5 Hz, $2H_{Major}$), 5.71–5.58 (m, $2H_{Major}$), 5.57–5.48 (m, $2H_{Minor}$), 4.14 (q, J = 7.0 Hz, $2H_{Major}$), 4.10–4.02 (m, $2H_{Minor}$), 3.86 (ddd, J = 7.9, 7.6, 5.7 Hz, $1H_{Minor}$), 3.58–3.48 (m, $1H_{Major}$), 3.05 (d, J = 6.5 Hz, 2H), 2.72 (dd, J = 15.3, 7.6 Hz, $1H_{Minor}$), 2.66 (dd, J = 15.3, 7.9 Hz, $1H_{Minor}$), 1.67 (dd, J = 4.8, 1.0 Hz, $3H_{Minor}$), 1.37 (d, J = 7.0 Hz, $3H_{Major}$), 1.26 (t, J = 7.2 Hz, $3H_{Major}$), 1.16 (t, J = 7.1 Hz, $3H_{Minor}$); δ_C (125 MHz, $CDCl_3$) 171.9, 171.5, 151.2, 149.0, 137.4, 132.5, 132.4, 131.8, 128.5, 128.2, 127.1, 122.4, 119.2, 119.0, 110.5, 110.1, 60.8, 60.7, 45.0, 42.4, 40.5, 38.0, 20.9, 18.1, 14.3, 14.3; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{18}NO_2$) requires m/z 244.1332, found m/z 244.1330.

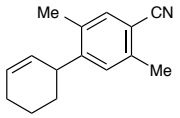


Major



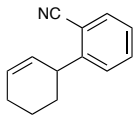
Minor

3-Methyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile and 2-methyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (Fig. 3b, Compound 29). Prepared according to the general procedure using 2-methylterephthalonitrile (107 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 2 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford an inseparable mixture of the *title compounds* (Combined yield: 123 mg, 0.623 mmol, 83%, 1.1:1.0) as a colorless oil; IR ν_{max}/cm^{-1} 2928, 2859, 2226, 1607, 1494, 1446, 1135, 885, 829, 721; δ_H (500 MHz, $CDCl_3$) 7.52 (d, *J* = 7.9 Hz, $1H_{Major}$), 7.44 (d, *J* = 7.9 Hz, $1H_{Minor}$), 7.42 (s, $1H_{Minor}$), 7.29 (d, *J* = 7.9 Hz, $1H_{Minor}$), 7.15 (s, $1H_{Major}$), 7.12 (d, *J* = 7.9 Hz, $1H_{Major}$), 6.00–5.94 (m, $1H_{Minor}$), 5.98–5.90 (m, $1H_{Major}$), 5.67–5.62 (m, $1H_{Major}$), 5.62–5.57 (m, $1H_{Minor}$), 3.67–3.61 (m, $1H_{Minor}$), 3.44–3.37 (m, $1H_{Major}$), 2.52 (s, $3H_{Major}$), 2.37 (s, $3H_{Minor}$), 2.14–2.06 (m, 4H), 2.04–1.96 (m, 2H), 1.77–1.68 (m, 2H), 1.68–1.58 (m, 2H), 1.55–1.47 (m, $1H_{Major}$), 1.47–1.38 (m, $1H_{Minor}$); δ_C (125 MHz, $CDCl_3$) 152.2, 150.3, 142.0, 137.0, 133.7 132.7, 129.9, 129.8, 129.7, 129.6, 129.0, 128.8, 128.5, 125.9, 119.5, 118.6, 110.3, 109.7, 42.0, 38.0, 32.4, 30.4, 25.0, 25.0, 21.1, 21.0, 20.7, 19.2; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{16}N$) requires m/z 198.1277, found m/z 198.1276.



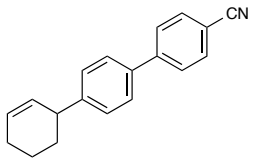
2,5-Dimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (Fig. 3b, Compound 30). Prepared according to the general procedure using 2,5-dimethylterephthalonitrile (117 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.),

triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 3 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford the *title compound* (117 mg, 0.554 mmol, 74%) as a colorless oil; IR ν_{max}/cm^{-1} 2956, 2917, 2854, 2218, 1611, 1496, 1445, 1395, 1247, 1128, 975, 906, 899, 884, 875, 736, 724; δ_H (500 MHz, $CDCl_3$) 7.36 (s, 1H), 7.11 (s, 1H), 6.00–5.94 (m, 1H), 5.62–5.56 (m, 1H), 3.63–3.56 (m, 1H), 2.47 (s, 3H), 2.32 (s, 3H), 2.15–2.08 (m, 2H), 2.02–1.94 (m, 1H), 1.76–1.68 (m, 1H), 1.68–1.58 (m, 1H), 1.46–1.37 (m, 1H); δ_C (125 MHz, $CDCl_3$) 150.1, 139.5, 133.9, 133.9, 129.5, 129.5, 129.2, 118.8, 110.0, 38.0, 30.4, 25.1, 21.1, 20.2, 18.7; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{18}N$) requires m/z 212.1434, found m/z 212.1432.

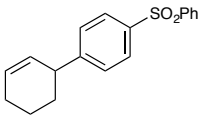


1',2',3',4'-Tetrahydro-[1,1'-biphenyl]-2-carbonitrile (Fig. 3b, Compound 31). Prepared according to the general procedure using phthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 4 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford the *title compound* (69 mg, 0.377 mmol, 50%) as a colorless oil; δ_H (500 MHz, $CDCl_3$) 7.62 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.53 (ddd, 8.0, 7.7, 1.4 Hz, 1H), 7.37 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.29 (ddd, *J* = 7.8, 7.7, 1.2 Hz, 1H), 6.02–5.97 (m, 1H), 5.67–5.61 (m, 1H), 3.90–3.83 (m, 1H), 2.18–2.08 (m, 3H), 1.78–1.63 (m, 2H), 1.58–1.49 (m, 1H); δ_C (125 MHz, $CDCl_3$) 150.4, 133.1, 132.9, 130.2, 128.4, 128.2, 126.7, 118.2, 112.1, 40.2, 31.7, 25.0, 21.0.

Data are consistent with those reported in the literature.[10]

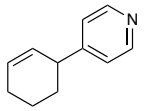


1'',2'',3'',4''-Tetrahydro-[1,1':4',1''-terphenyl]-4-carbonitrile (Fig. 3b, Compound 32). Prepared according to the general procedure using 4,4-biphenylcarbonitrile (153 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 5 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford the *title compound* (129 mg, 0.497 mmol, 66%) as a colorless crystalline solid; IR ν_{max}/cm^{-1} 2923, 2855, 2222, 1605, 1490, 1444, 1395, 1178, 1005, 906, 851, 818, 725; δ_H (500 MHz, $CDCl_3$) 7.71 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 5.98–5.87 (m, 1H), 5.76–5.68 (m, 1H), 3.51–3.43 (m, 1H), 2.14–2.08 (m, 2H), 2.09–2.02 (m, 1H), 1.81–1.72 (m, 1H), 1.70–1.53 (m, 2H); δ_C (125 MHz, $CDCl_3$) 147.7, 145.7, 137.0, 132.7, 129.8, 129.0, 128.7, 127.7, 127.3, 119.2, 110.7, 41.7, 32.7, 25.1, 21.3; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}N$) requires m/z 260.1434, found m/z 260.1433.



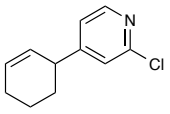
4'-(Phenylsulfonyl)-1,2,3,4-tetrahydro-1,1'-biphenyl (Fig. 3b, Compound 33). Prepared according to the general procedure using 4-(phenylsulfonyl)benzonitrile (182 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (51.8 mg, 0.375 mmol, 0.50 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 5 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to afford the *title compound* (154 mg, 0.516 mmol, 69%) as a colorless crystalline solid; IR ν_{max}/cm^{-1} 2936, 1592, 1447, 1306, 1154, 1107, 1071, 832, 744, 719, 685; δ_H (500 MHz, $CDCl_3$) 7.97–7.92 (m, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.58–7.53 (m, 1H), 7.52–7.48 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 5.97–5.89 (m, 1H),

5.65–5.60 (m, 1H), 3.48–3.40 (m, 1H), 2.12–2.04 (m, 2H), 2.04–1.94 (m, 1H), 1.75–1.65 (m, 1H), 1.67–1.54 (m, 1H), 1.54–1.43 (m, 1H); δ_C (125 MHz, $CDCl_3$) 152.8, 142.1, 139.2, 133.1, 129.7, 129.4, 128.8, 128.7, 127.9, 127.7, 41.9, 32.4, 25.0, 21.0; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{19}O_2S$) requires m/z 299.1100, found m/z 299.1101.



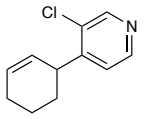
4-(Cyclohex-2-en-1-yl)pyridine (Fig. 3b, Compound 34). Prepared according to the general procedure using 4-cyanopyridine (78.0 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 4 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 1:1) to afford the *title compound* (100 mg, 0.628 mmol, 84%) as a colorless oil; δ_H (500 MHz, $CDCl_3$) 8.50 (d, J = 5.4 Hz, 2H), 7.14 (d, J = 5.4 Hz, 2H), 5.99–5.91 (m, 1H), 5.69–5.62 (m, 1H), 3.42–3.34 (m, 1H), 2.13–2.05 (m, 2H), 2.05–1.96 (m, 1H), 1.77–1.66 (m, 1H), 1.66–1.57 (m, 1H), 1.57–1.48 (m, 1H); δ_C (125 MHz, $CDCl_3$) 155.5, 149.8, 129.8, 128.3, 123.3, 41.2, 31.9, 25.0, 21.0.

Data are consistent with those reported in the literature.[11]



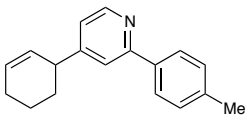
2-Chloro-4-(cyclohex-2-en-1-yl)pyridine (Fig. 3b, Compound 35). Prepared according to the general procedure using 2-chloro-4-cyanopyridine (104 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (25.9 mg, 0.188 mmol, 0.25 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 4 hours, the reaction mixture was concentrated, then the crude

material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 9:1) to afford the *title compound* (106 mg, 0.547 mmol, 73%) as a colorless oil; IR ν_{max}/cm^{-1} 2931, 1590, 1543, 1379, 1085, 837, 733; δ_H (500 MHz, $CDCl_3$) 8.28 (d, *J* = 5.2 Hz, 1H), 7.19 (d, *J* = 1.5 Hz, 1H), 7.08 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.02–5.94 (m, 1H), 5.67–5.59 (m, 1H), 3.43–3.35 (m, 1H), 2.14–2.06 (m, 2H), 2.07–1.98 (m, 1H), 1.77–1.67 (m, 1H), 1.67–1.57 (m, 1H), 1.58–1.47 (m, 1H); δ_C (125 MHz, $CDCl_3$) 159.1, 151.7, 149.6, 130.5, 127.4, 123.7, 122.2, 41.1, 31.8, 24.9, 20.8; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{13}{}^{35}ClN$) requires m/z 194.0730, found m/z 194.0731.



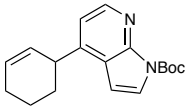
3-Chloro-4-(cyclohex-2-en-1-yl)pyridine (Fig. 3b, Compound 36). Prepared according to the general procedure using 3-chloro-4-cyanopyridine (104 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 24 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 4:1) to afford the *title compound* (101 mg, 0.521 mmol, 70%) as a colorless oil; δ_H (500 MHz, $CDCl_3$) 8.52 (br s, 1H), 8.40 (d, *J* = 5.0 Hz, 1H), 7.20 (d, *J* = 5.0 Hz, 1H), 6.06–6.00 (m, 1H), 5.63–5.58 (m, 1H), 3.88–3.81 (m, 1H), 2.15–2.04 (m, 3H), 1.73–1.60 (m, 2H), 1.53–1.44 (m, 1H); δ_C (125 MHz, $CDCl_3$) 152.2, 149.4, 147.9, 131.9, 130.7, 127.3, 123.9, 37.7, 29.3, 25.0, 20.6.

Data are consistent with those reported in the literature.[12]

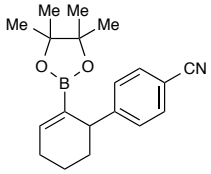


4-(Cyclohex-2-en-1-yl)-2-(*p*-tolyl)pyridine (Fig. 3b, Compound 37). Prepared according to the general procedure using 2-(*p*-tolyl)-4-cyanopyridine (146 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2

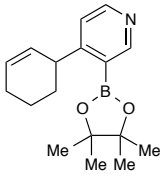
mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 7 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1) to afford the *title compound* (150 mg, 0.602 mmol, 80%) as a colorless oil; IR ν_{max}/cm^{-1} 2926, 1597, 1551, 1469, 1416, 817; δ_H (500 MHz, $CDCl_3$) 8.58 (d, *J* = 5.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.56 (br s, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.10 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.02–5.96 (m, 1H), 5.74–5.69 (m, 1H), 3.49–3.43 (m, 1H), 2.41 (s, 3H), 2.16–2.10 (m, 2H), 2.10–2.03 (m, 1H), 1.80–1.72 (m, 1H), 1.71–1.55 (m, 2H); δ_C (125 MHz, $CDCl_3$) 157.4, 156.7, 149.2, 139.1, 136.6, 129.9, 129.6, 128.3, 127.0, 121.7, 120.1, 41.6, 32.0, 25.0, 21.4, 21.1; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{20}N$) requires m/z 250.1590, found m/z 250.1588.



***tert*-Butyl-4-(cyclohex-2-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate (Fig. 3b, Compound 38)**. Prepared according to the general procedure using *tert*-butyl 4-cyano-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate (182 mg, 0.750 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (8.1 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 5 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1 → 9:1) to afford the *title compound* (156 mg, 0.523 mmol, 70%) as a colorless oil; IR ν_{max}/cm^{-1} 2932, 1757, 1727, 1401, 1388, 1318, 1298, 1252, 1126, 725; δ_H (500 MHz, $CDCl_3$) 8.42 (d, *J* = 5.0 Hz, 1H), 7.59 (d, *J* = 4.1 Hz, 1H), 7.04 (d, *J* = 5.0 Hz, 1H), 6.60 (d, *J* = 4.1 Hz, 1H), 6.03–5.95 (m, 1H), 5.78–5.71 (m, 1H), 3.81–3.73 (m, 1H), 2.18–2.11 (m, 2H), 2.11–2.04 (m, 1H), 1.80–1.72 (m, 1H), 1.73–1.63 (m, 11H); δ_C (125 MHz, $CDCl_3$) 148.6, 148.3, 148.1, 145.4, 129.5, 128.5, 125.7, 122.0, 117.4, 103.0, 84.0, 39.2, 30.7, 28.3, 25.1, 21.3; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{23}N_2O_2$) requires m/z 299.1754, found m/z 299.1755.

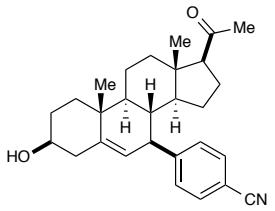


6'-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (Fig. 4a, Compound 39). Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), 2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (780 mg, 3.75 mmol, 5 equivs.), triisopropylsilanethiol (16.1 μL, 0.075 mmol, 0.10 equivs.) and acetone (7.5 mL). After 24 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (Iatrobeads, Hexanes/Et_2O – 19:1) to afford the *title compound* and minor uncharacterized isomeric products (170 mg, 0.550 mmol, 73%, 6:1) as a colorless oil; IR ν_{max}/cm^{-1} 2978, 2932, 2227, 1631, 1606, 1373, 1316, 1142, 910, 852, 729; δ_H (500 MHz, $CDCl_3$) 7.54 (d, *J* = 8.2, 2H), 7.28 (d, *J* = 8.2, 2H), 6.82–6.79 (m, 1H), 3.66–3.59 (m, 1H), 2.23–2.10 (m, 2H), 2.01–1.91 (m, 1H), 1.61–1.49 (m, 3H), 1.11 (s, 6H), 0.94 (s, 6H); δ_C (125 MHz, $CDCl_3$) 153.4, 144.6, 131.9, 129.2, 119.6, 109.4, 83.2, 42.4, 32.1, 26.5, 25.0, 24.1, 19.2 (Signal for boron-substituted carbon not observed); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{25}{}^{10}BNO_2$) requires m/z 309.2009, found m/z 309.2008.



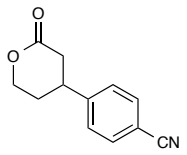
4-(Cyclohex-2-en-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (Fig. 4a, Compound 40). Prepared according to the general procedure using 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isonicotinonitrile (173 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (21.0 mg, 0.150 mmol, 0.20 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (380 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (16.1 μL, 0.075 mmol, 0.10 equivs.) and acetone (7.5 mL). After 24 hours, the reaction mixture was concentrated, then the crude material was dissolved in

pentane and filtered. The filtrate was concentrated *in vacuo* to afford a pale yellow solid that was flushed through a pad of Florisil (20 × 5 mm) eluting with EOAc to afford the *title compound* (128 mg, 0.449 mmol, 60%) as an off-white solid; IR ν_{max}/cm^{-1} 2977, 2929, 1585, 1356, 1144, 1103, 1036, 671; δ_H (500 MHz, $CDCl_3$) 8.85 (br s, 1H), 8.54 (br s, 1H), 7.21 (d, *J* = 5.2 Hz, 1H), 6.01–5.93 (m, 1H), 5.70–5.63 (m, 1H), 4.19–4.11 (m, 1H), 2.12–1.99 (m, 3H), 1.73–1.56 (m, 2H), 1.46–1.37 (m, 1H), 1.35 (s, 12H); δ_C (125 MHz, $CDCl_3$) 162.8, 155.7, 151.0, 129.5, 129.0, 122.6, 84.1, 39.5, 32.8, 25.1, 25.1, 24.8, 20.9 (Signal for boron-substituted carbon not observed); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{25}{}^{10}BNO_2$) requires m/z 285.2009, found m/z 285.2005.

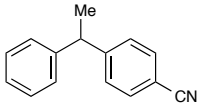


4-((3*S*,7*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-Acetyl-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-7-yl)benzonitrile (Fig. 4b, Compound 41). Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 µmol, 0.01 equivs.), 5-pregnen-3β-ol-20-one (237 mg, 0.75 mmol, 1.00 equivs.), triisopropylsilanethiol (16.1µL, 0.075 mmol, 0.10 equivs.) and acetone (7.5 mL). After 3 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (Iatrobeads, Hexanes/EtOAc – 2:1) to give a colorless foam. The material was dissolved in MeOH/H_2O (1:1, 5 mL) then concentrated *in vacuo* to afford an inseparable mixture of the *title compound* and a minor uncharacterized isomer (211 mg, 0.505 mmol, 67%, >10:1) as an off-white solid; IR ν_{max}/cm^{-1} 3382 (br), 2966, 2927, 2230, 1699, 1360, 1054, 828; δ_H (500 MHz, $CDCl_3$) 7.55 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 4.99–4.94 (m, 1H), 3.60–3.49 (m, 1H), 3.09 (d, *J* = 9.1 Hz, 1H), 2.42 (t, *J* = 9.4 Hz, 1H), 2.23 (d, *J* = 8.0 Hz, 2H), 2.09 (s, 3H), 2.09–2.02 (m, 1H), 1.97–1.85 (m, 4H), 1.77–1.69 (m, 1H), 1.60–1.41 (m, 4H), 1.33 (ddd, *J* = 12.6, 10.7, 7.3 Hz, 1H), 1.27–1.10 (m, 3H), 1.17 (s, 3H), 0.58 (s, 3H), 0.50–0.39 (m, 1H); δ_C (125 MHz, $CDCl_3$) 209.5, 152.8, 140.8, 132.4, 129.4, 125.6, 119.2, 110.1, 71.5, 63.0, 57.2, 50.9, 49.9, 44.7, 42.0, 38.7, 38.6, 37.3, 36.3, 31.7, 31.7, 27.0, 23.3, 21.3,

19.9, 13.4; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{28}H_{36}NO_2$) requires m/z 418.2741, found m/z 418.2742.



4-(2-Oxotetrahydro-2*H*-pyran-4-yl)benzonitrile (Fig. 4c). Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), potassium carbonate (5.2 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), *tert*-butyl-(3,4-dihydro-2*H*-pyran-6-yl)oxy)dimethylsilane (189 μL, 0.825 mmol, 1.10 equivs.), triisopropylsilanethiol (8.05 μL, 0.038 mmol, 0.05 equivs.) and acetone (7.5 mL). After 3 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 3:2) to afford the *title compound* (103 mg, 0.512 mmol, 68%) as a pale yellow solid; IR ν_{max}/cm^{-1} 2225, 1727, 1399, 1217, 1075, 838; δ_H (500 MHz, $CDCl_3$) 7.67 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 4.53 (ddd, J = 11.4, 4.9, 3.7 Hz, 1H), 4.41 (ddd, J = 11.4, 11.1, 3.7 Hz, 1H), 3.32 (dddd, J = 10.7, 10.5, 6.1, 4.7 Hz, 1H), 2.94 (ddd, J = 17.6, 6.1, 1.7 Hz, 1H), 2.61 (dd, J = 17.6, 10.5 Hz, 1H), 2.25–2.16 (m, 1H), 2.05 (dddd, J = 14.0, 11.1, 10.7, 4.9 Hz, 1H); δ_C (125 MHz, $CDCl_3$) 169.8, 148.1, 133.0, 127.5, 118.6, 111.5, 68.4, 37.7, 37.1, 30.0; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{12}NO_2$) requires m/z 202.0863, found m/z 202.0863.



4-(1-Phenylethyl)benzonitrile (Fig. 4d). Prepared according to the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), sodium carbonate (4.0 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), ethylbenzene (459 μL, 3.75 mmol, 5.00 equivs.), triisopropylsilanethiol (16.1 μL, 0.075 mmol, 0.10 equivs.) and acetone (7.5 mL). After 3 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to afford the *title compound* (107 mg, 0.516

mmol, 69%) as a pale yellow oil; δ_H (500 MHz, $CDCl_3$) 7.57 (d, *J* = 8.5 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 4H), 7.26–7.19 (m, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 152.0, 144.8, 132.4, 128.8, 128.6, 127.7, 126.8, 119.2, 110.1, 45.0, 21.6.

Data are consistent with those reported in the literature.[13]

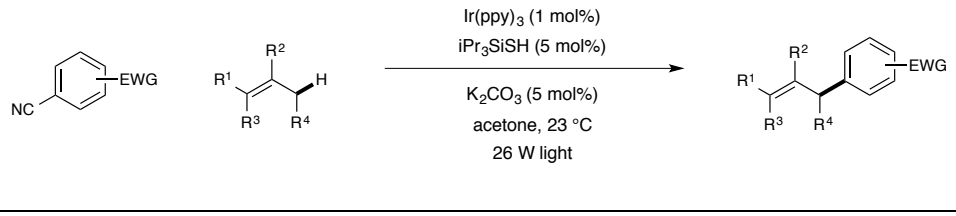
Competition Experiment (Fig. 4e)

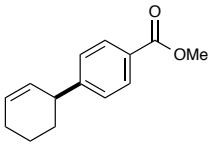
Following the general procedure using terephthalonitrile (96 mg, 0.75 mmol, 1.00 equivs.), sodium carbonate (4.0 mg, 0.038 mmol, 0.05 equivs.), *tris*[2-phenylpyridinato-C^2,*N*]iridium(III) (4.9 mg, 7.50 μmol, 0.01 equivs.), cyclohexene (190 μL, 1.88 mmol, 2.50 equivs.), ethylbenzene (230 μL, 1.88 mmol, 2.50 equivs.), triisopropylsilanethiol (16.1 μL, 0.075 mmol, 0.10 equivs.) and acetone (7.5 mL). After 3 hours, the reaction mixture was concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 49:1) to exclusively afford *1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile* (107 mg, 0.584 mmol, 78%) as a colourless oil.

Data are consistent with those reported previously.

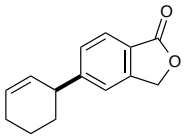
VI. Additional Allylic Arylation Examples

Additional products that can be accessed under the standard reaction conditions are included below. The reported yields are based on ^{1}H NMR spectroscopic analysis of the unpurified reaction mixtures and are unoptimised.

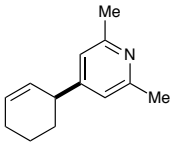




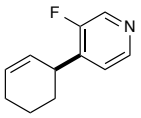
32%



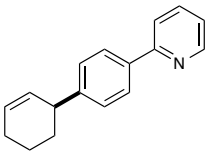
27%



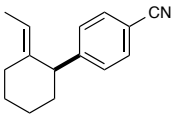
18%



14%



26%



63% (5 Isomers)

[a] All reactions were run on 0.25 mmol scale for 24 h.

[b] % Yields were calculated by ^{1}H NMR spectroscopy using 1,3-bis(trifluoromethyl)-5-bromobenzene (0.25 mmol) as an internal standard.

VII. References

1. Perrin, D.D. & Armarego, W.L.F. *Purification of Laboratory Chemicals, 3rd ed.* Pergamon Press: Oxford, 1988.

2. Pangborn, A.B., Giardello, M.A., Grubbs, R.H., Rosen, R.K. & Timmers, F.J. Safe and convenient procedure for solvent purification. *Organometallics* **15**, 1518–1520 (1996).

3. Still, W.C., Kahn, M. & Mitra, A. Rapid chromatographic technique for preparative separations with moderate resolution. *J. Org. Chem.* **43**, 2923–2925 (1978).

4. Fleckenstein, C.A. & Plenio, H. Highly efficient Suzuki-Miyaura coupling of heterocyclic substrates through rational reaction design. *Chem. Eur. J.* **14**, 4267–4279 (2008).

5. Han, X., Zhang, Y. & Wu. J. Mild two-step process for the transition-metal-free synthesis of carbon–carbon bonds from allylic alcohols/ethers and Grignard reagents. *J. Am. Chem. Soc.* **132**, 4104–4106 (2010).

6. Mangion, D., Kendall, J. & Arnold, D.R. Photosensitized (electron-transfer) deconjugation of 1-arylcyclohexenes. *Org. Lett.* **3**, 45–48 (2001).

7. Roth, H.D., Weng, H., Zhou, D. & Lakkaraju, P.S. Medium- and sensitizer-dependent radical cation reactions: Deprotonation in fluid solution and solid matrices. *Acta. Chem. Scan.* **51**, 626–635 (1997).

8. E. Romney, D.K. & Miller, S.J. A peptide-embedded trifluoromethyl ketone catalyst for enantioselective epoxidation. *Org. Lett.* **14**, 1138–1141 (2012).

9. Nakao, Y. *et al.* Organo[2-(hydroxymethyl)phenyl]dimethylsilanes as mild and reproducible agents for rhodium-catalysed 1,4-additions. *J. Am. Chem. Soc.* **129**, 9137-9143 (2007).

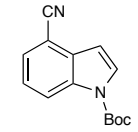
10. Borg. R.M., Arnold, D.R. & Cameron, T.S. Radical ions in photochemistry. 15. The photosubstitution reaction between dicyanobenzenes and alkyl olefins. *Can. J. Chem.* **62**, 1785–1802 (1984).

11. Hoshikawa, T. & Inoue, M. Photoinduced direct 4-pyridination of C(sp^3)–H bonds. *Chem. Sci.* **4**, 3118-3123 (2013).

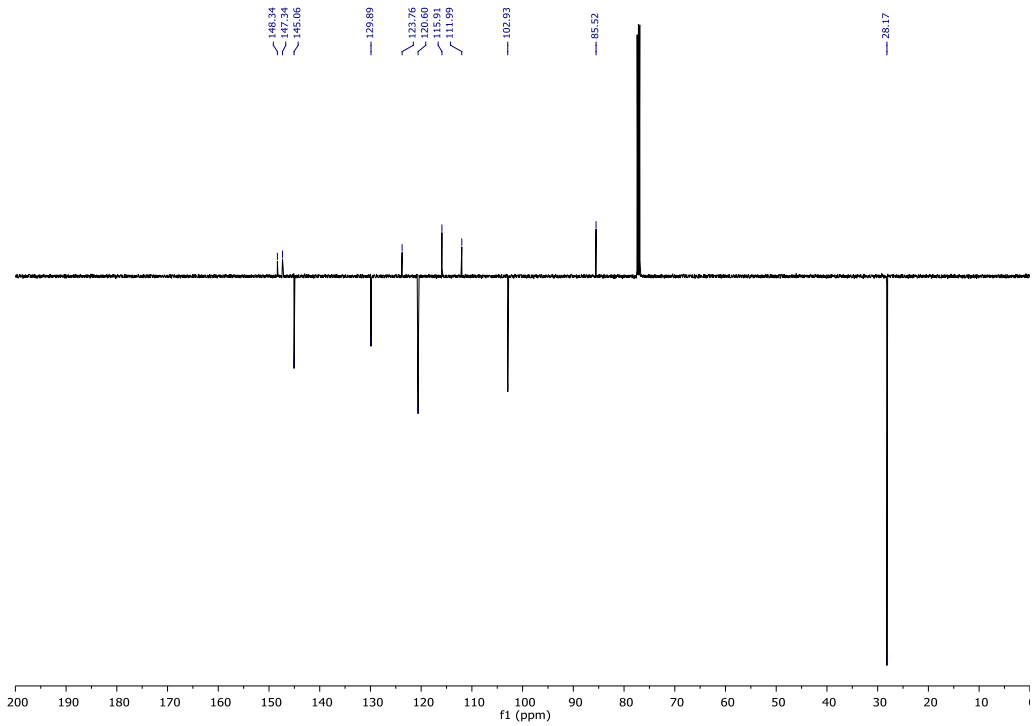
12. Jeganmohan, M. & Knochel, P. $tmpr_4Zr$: An atom-economical base for the metalation of functionalized arenes and heteroarenes. *Angew. Chem. Int. Ed.* **49**, 8520–8524 (2010).

13. Amatore, M. & Gosmini, C. Synthesis of functionalised diarylmethanes *via* a cobalt-catalysed cross-coupling of arylzinc species with benzyl chlorides. *Chem. Commun*. 5019–5021 (2008).

VIII. NMR Spectra



500 MHz, $CDCl_3$



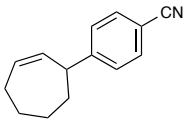
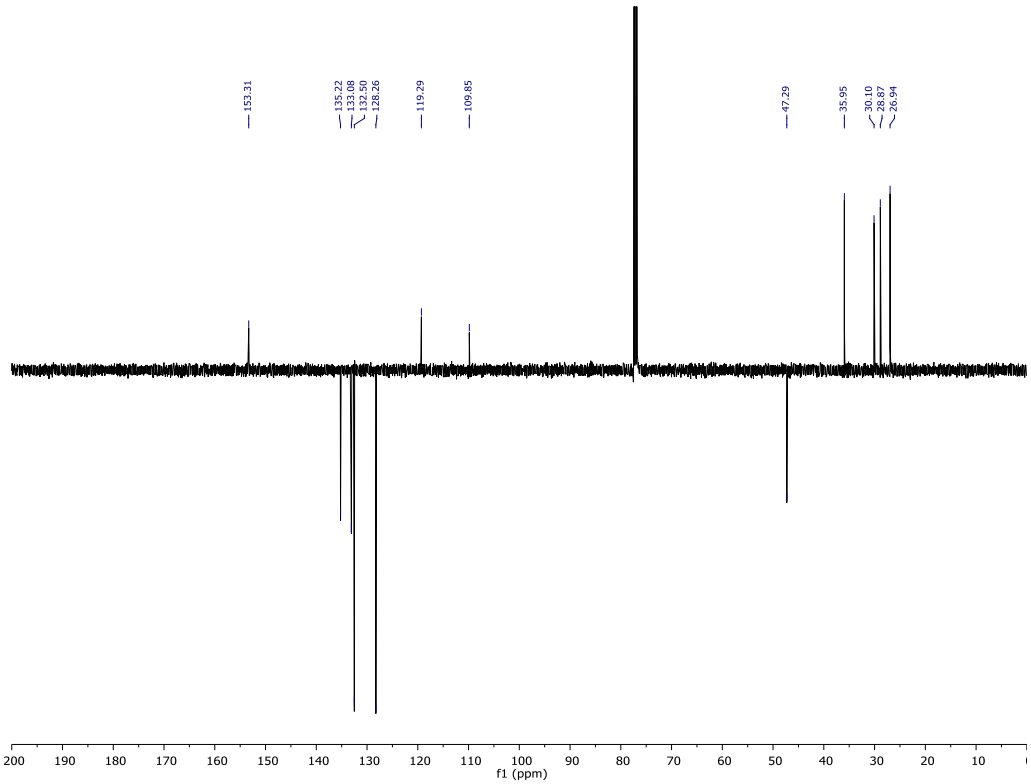


Fig. 3a, Compound **14**

(500 MHz, $CDCl_3$)



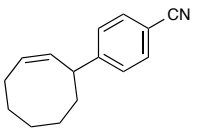
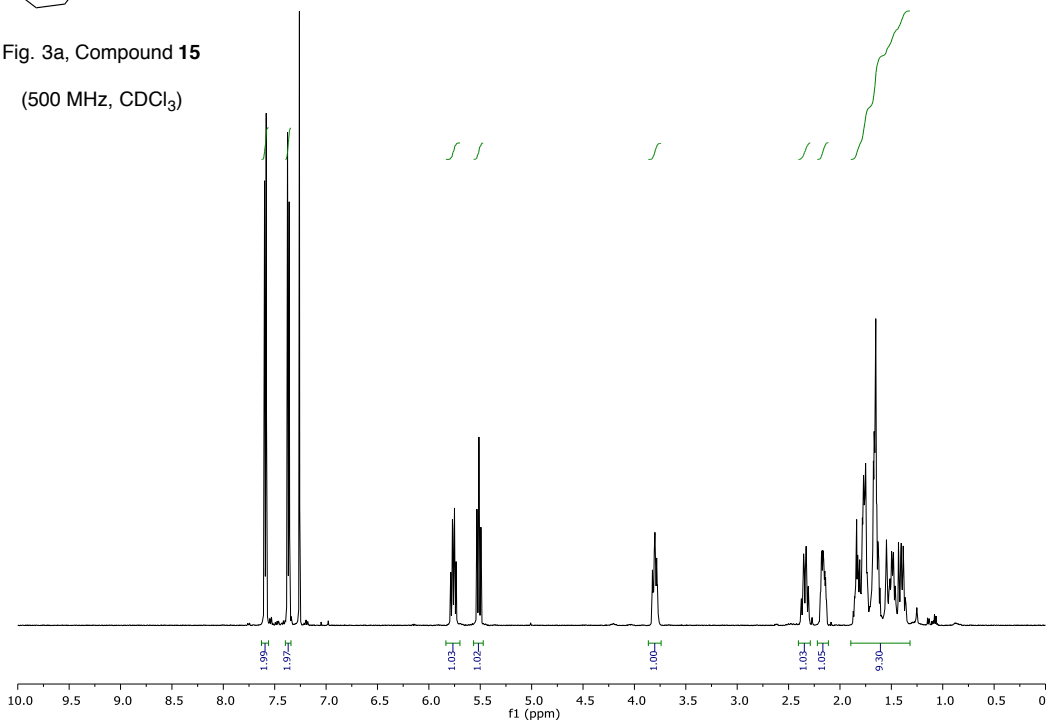
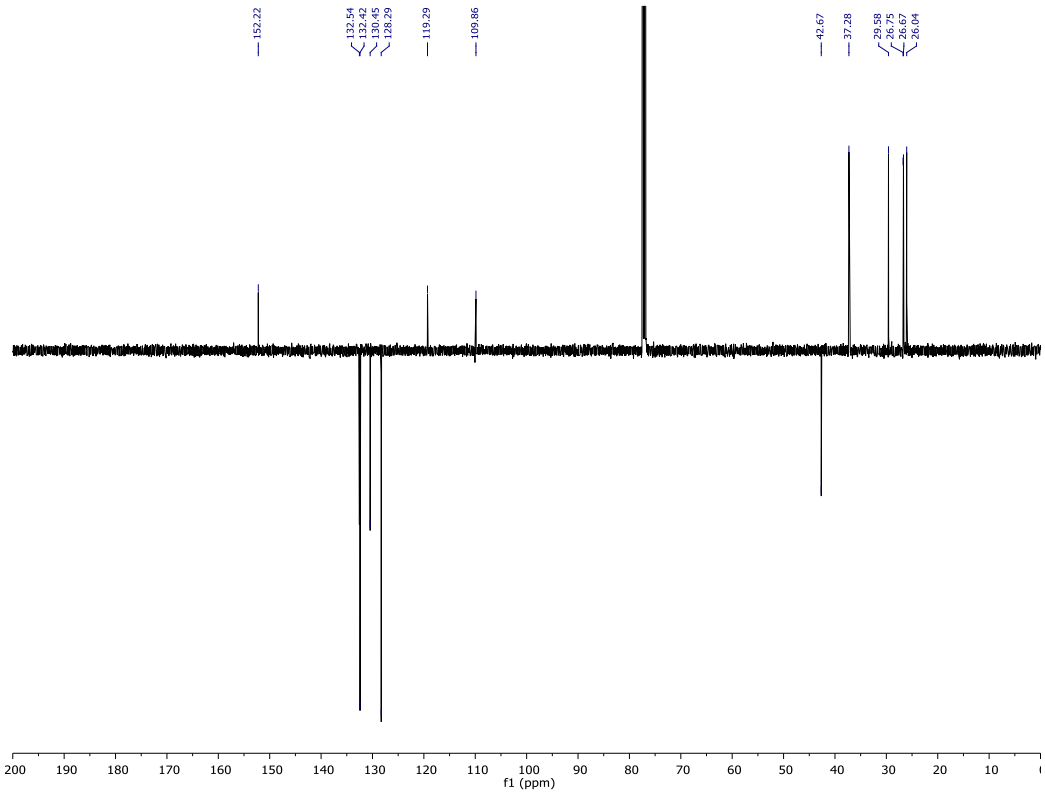


Fig. 3a, Compound **15**

(500 MHz, $CDCl_3$)





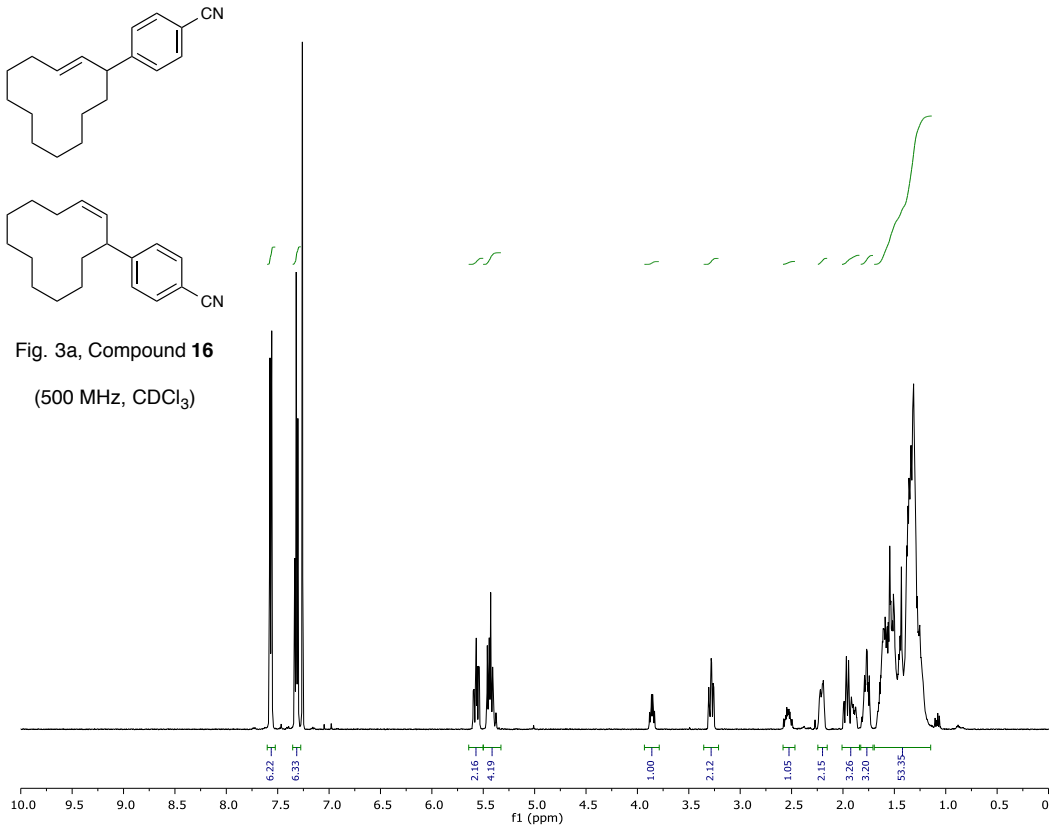
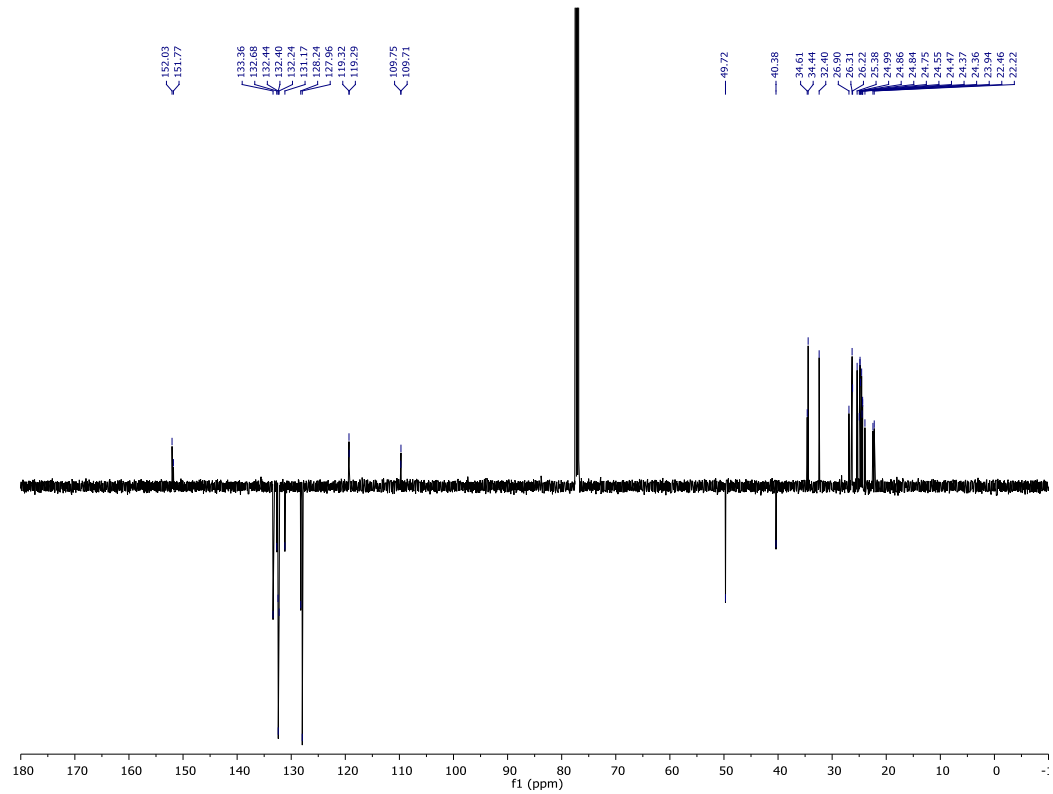


Fig. 3a, Compound **16**

(500 MHz, $CDCl_3$)



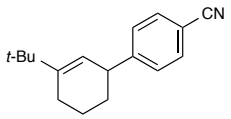
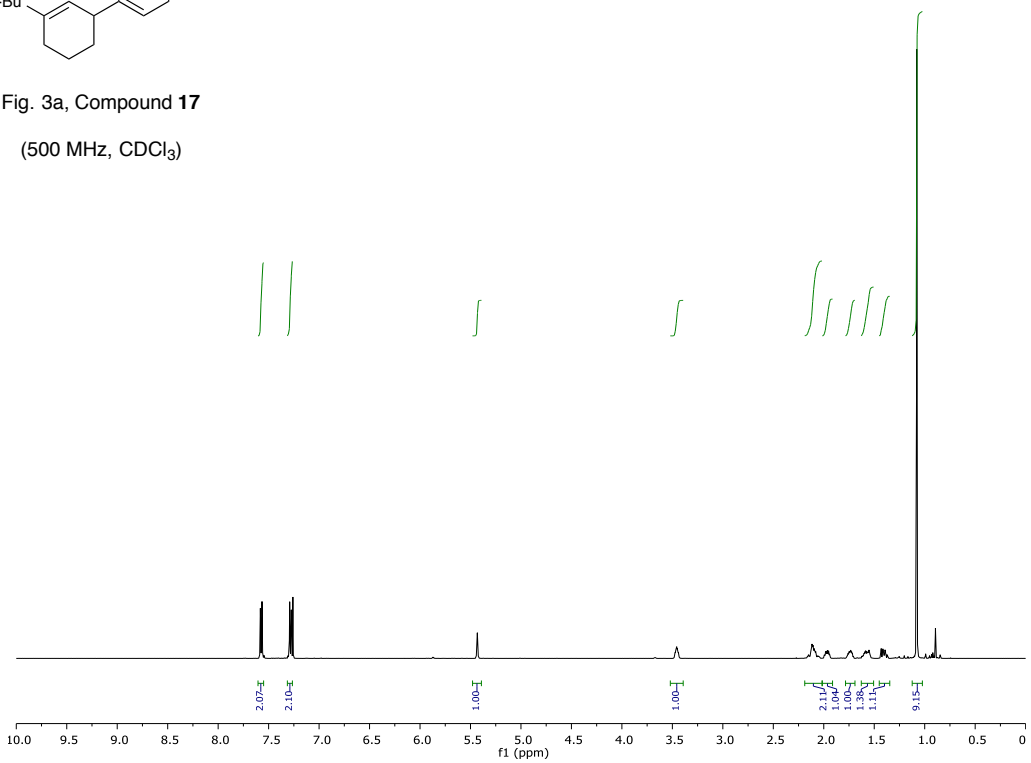
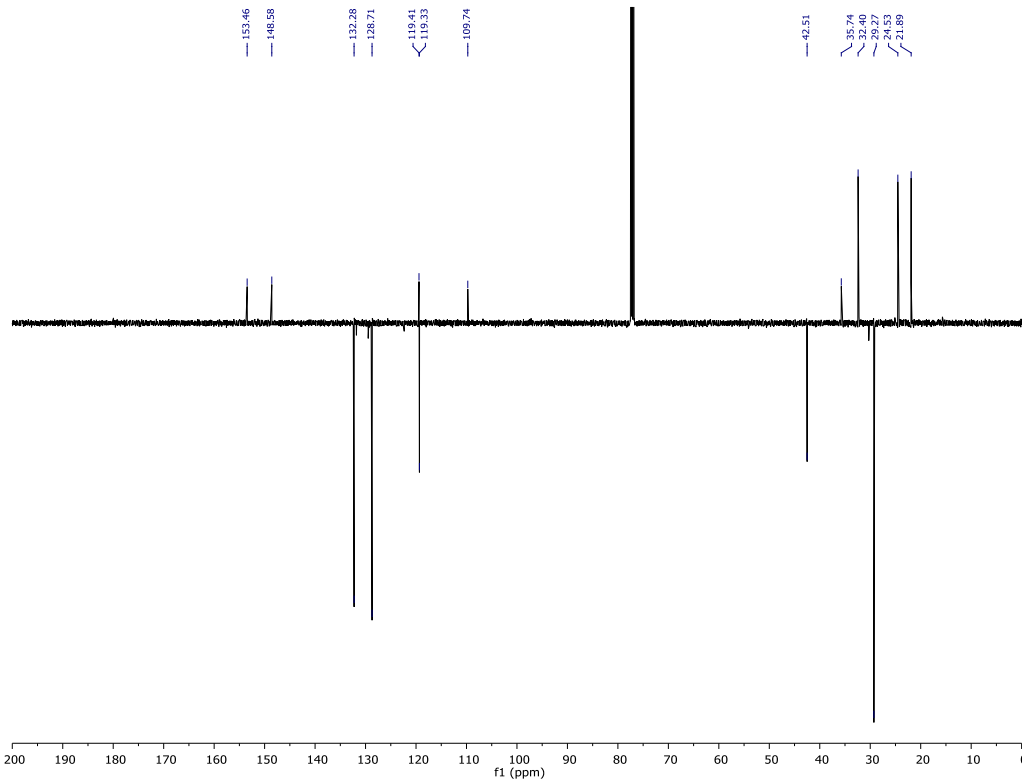


Fig. 3a, Compound **17**

(500 MHz, $CDCl_3$)





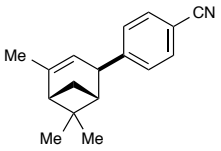
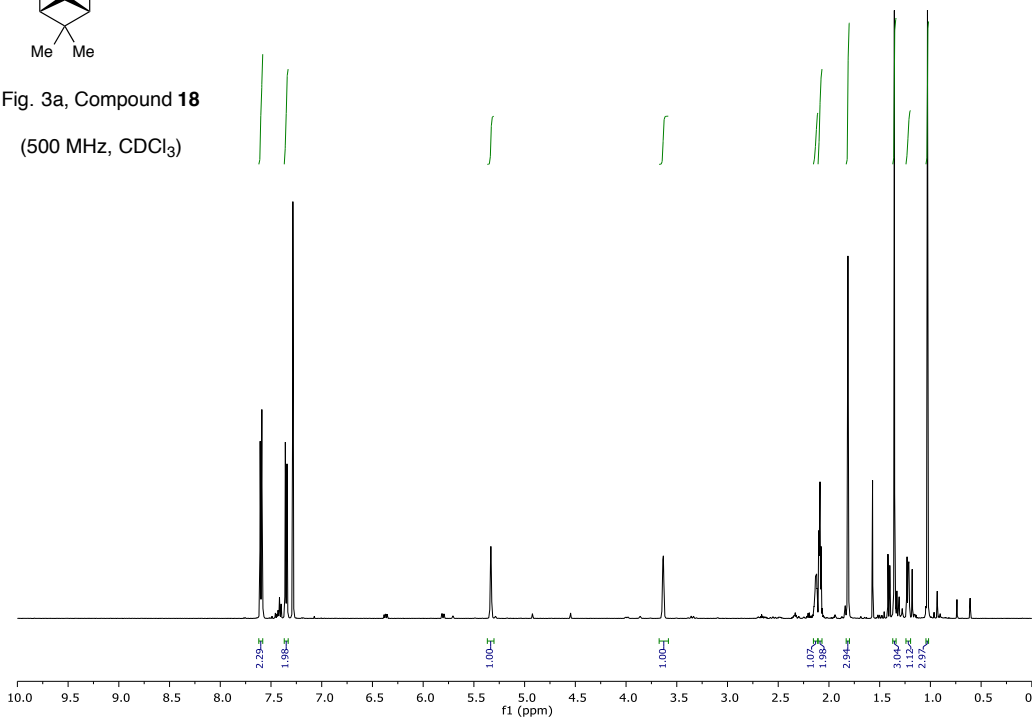
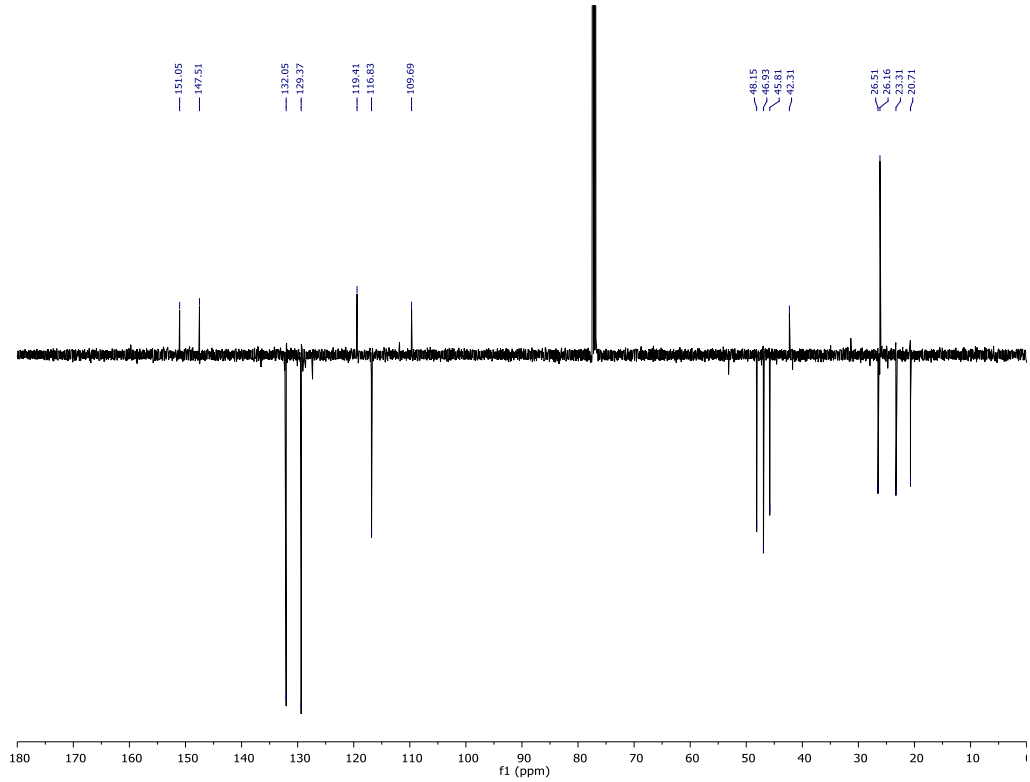


Fig. 3a, Compound **18**

(500 MHz, $CDCl_3$)





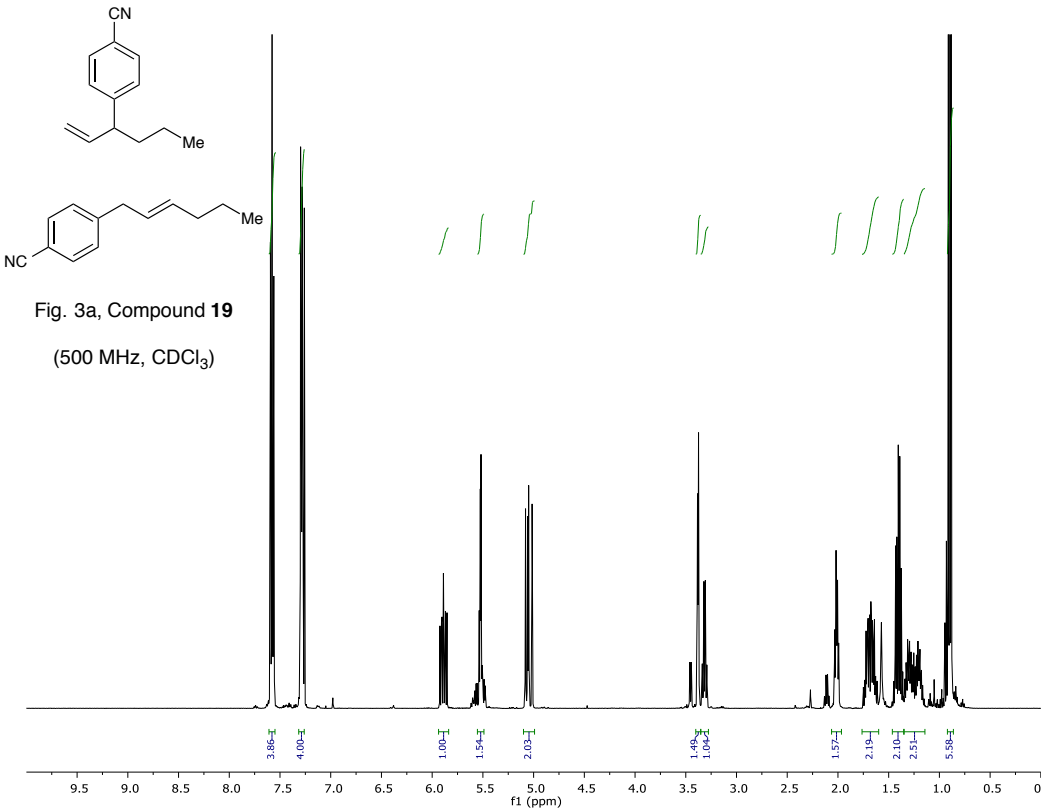
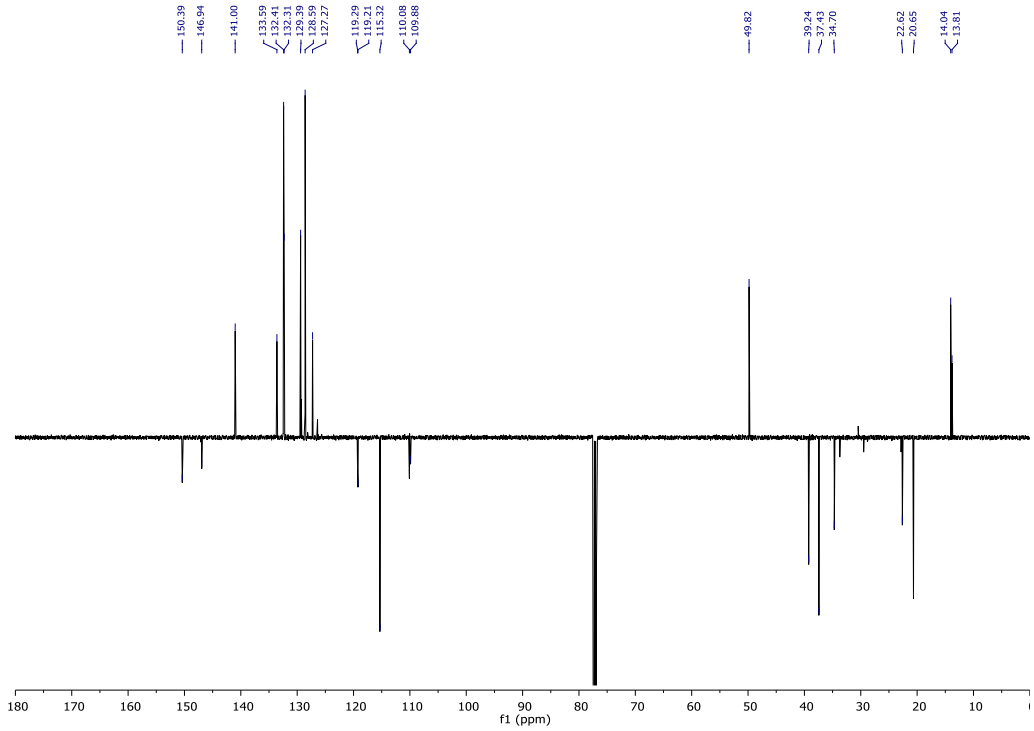


Fig. 3a, Compound **19**

(500 MHz, $CDCl_3$)



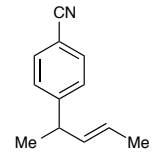
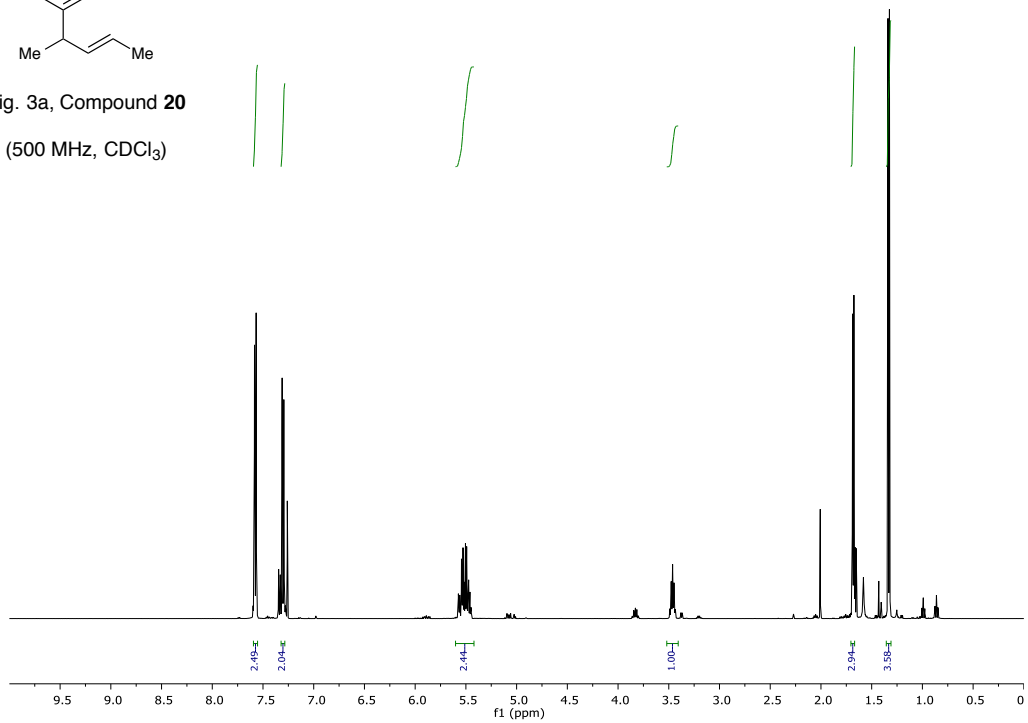
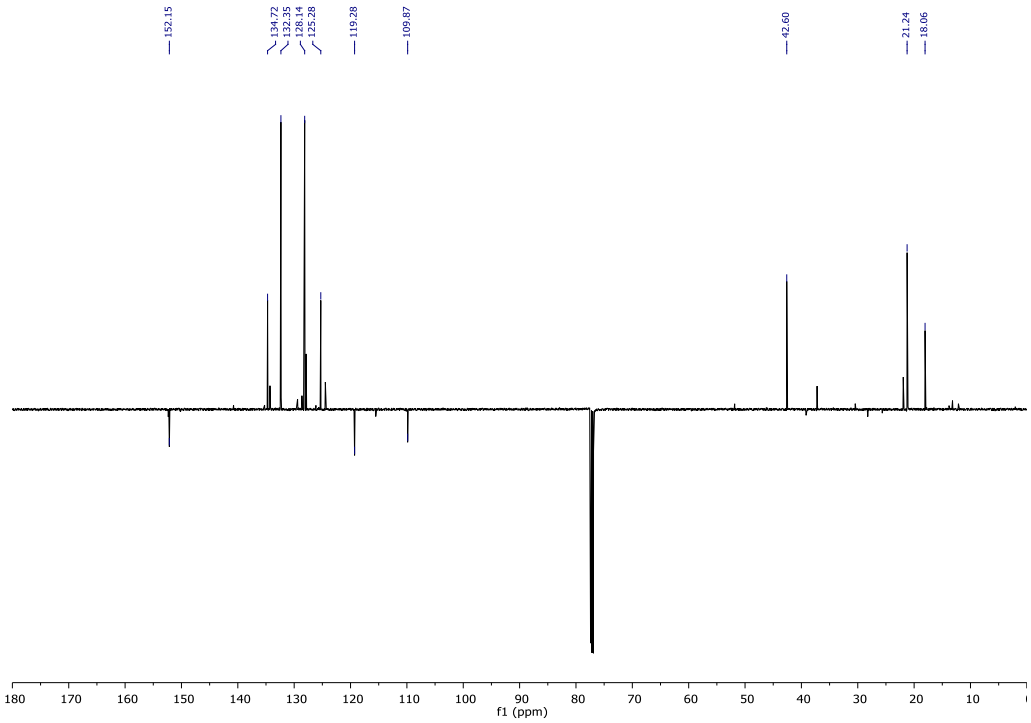


Fig. 3a, Compound **20**

(500 MHz, $CDCl_3$)





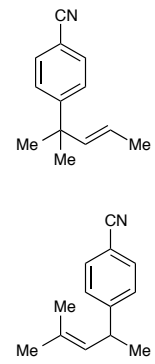
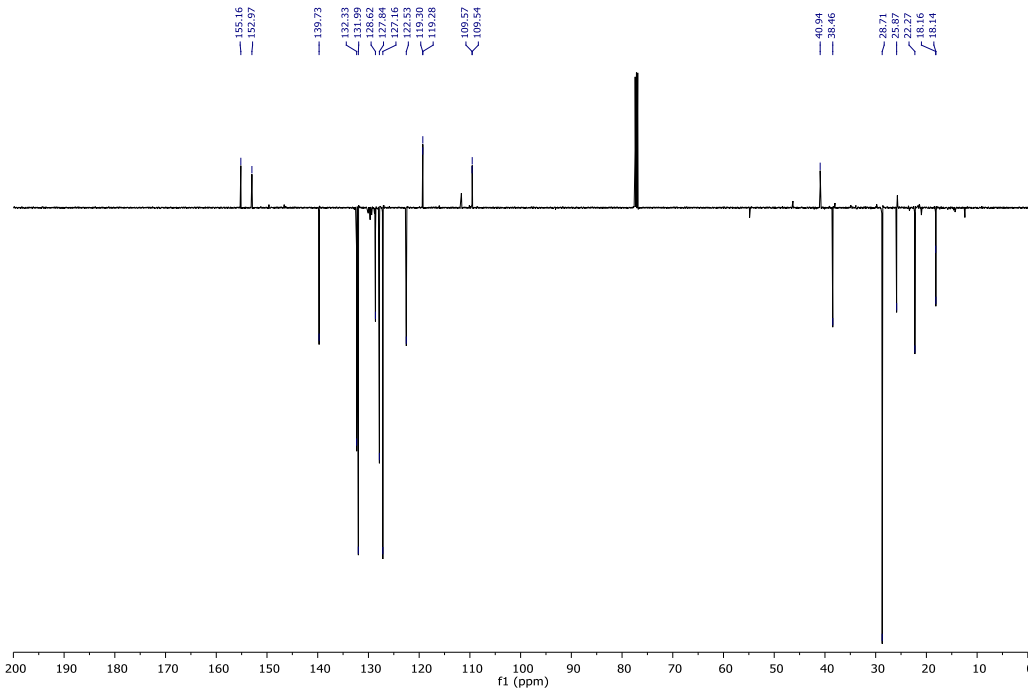


Fig. 3a, Compound **21**

(500 MHz, $CDCl_3$)



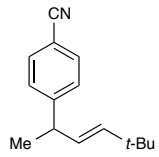
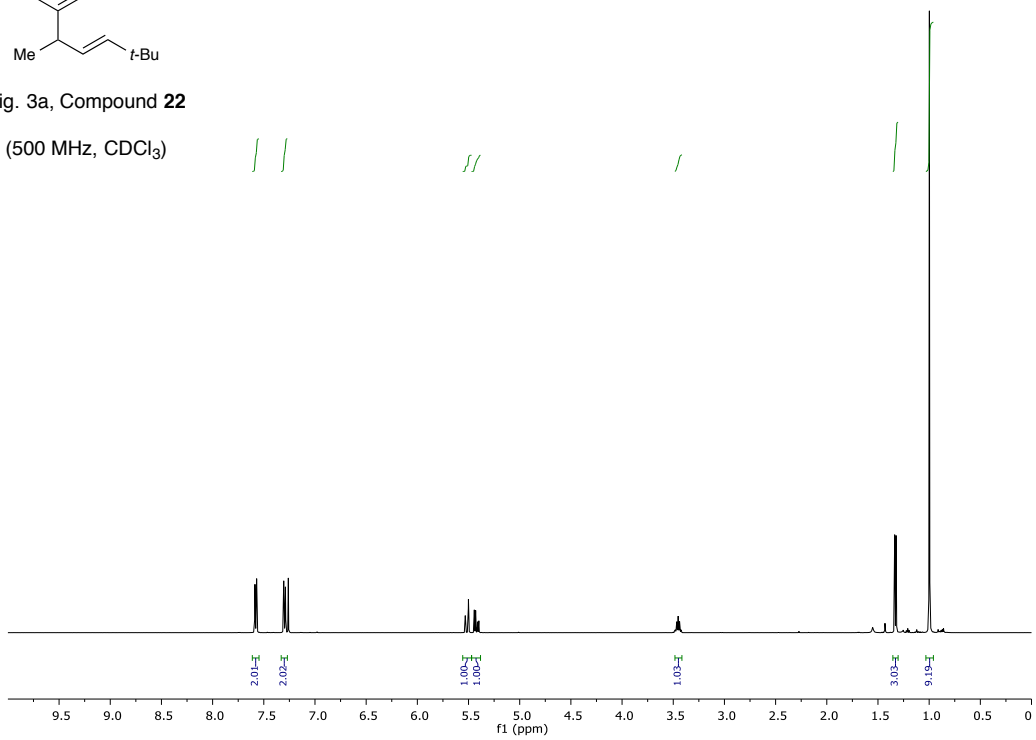
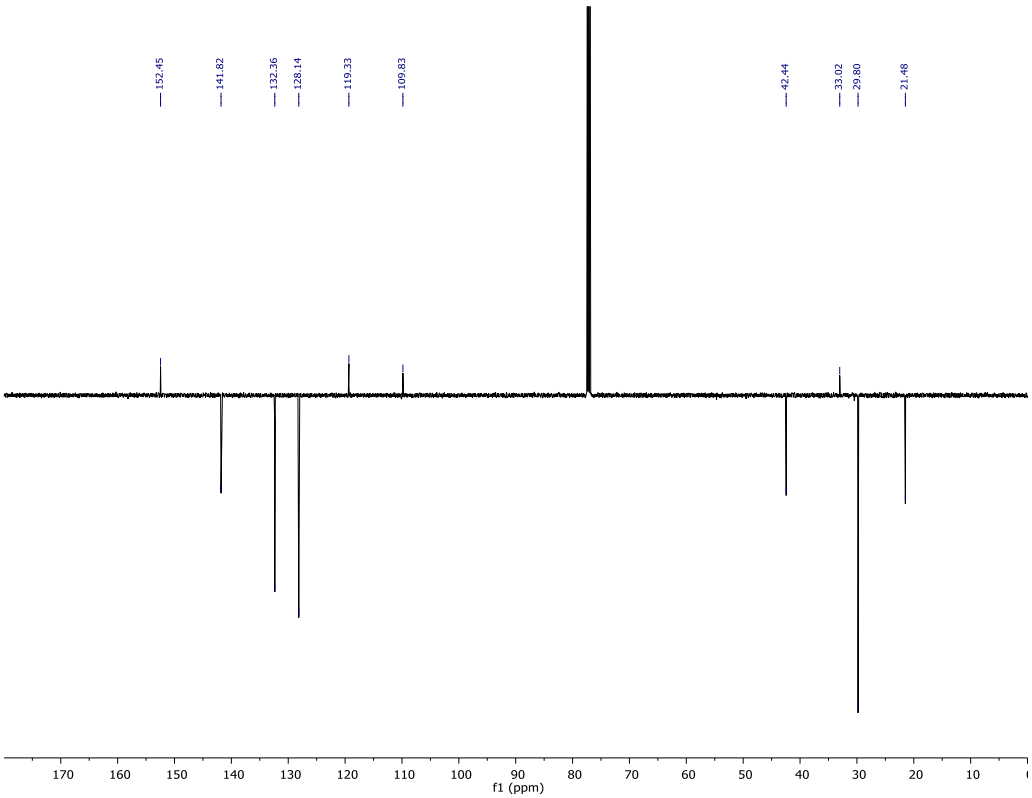


Fig. 3a, Compound **22**

(500 MHz, $CDCl_3$)





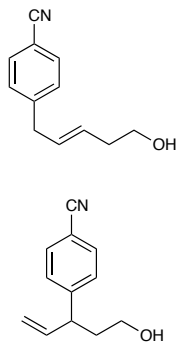
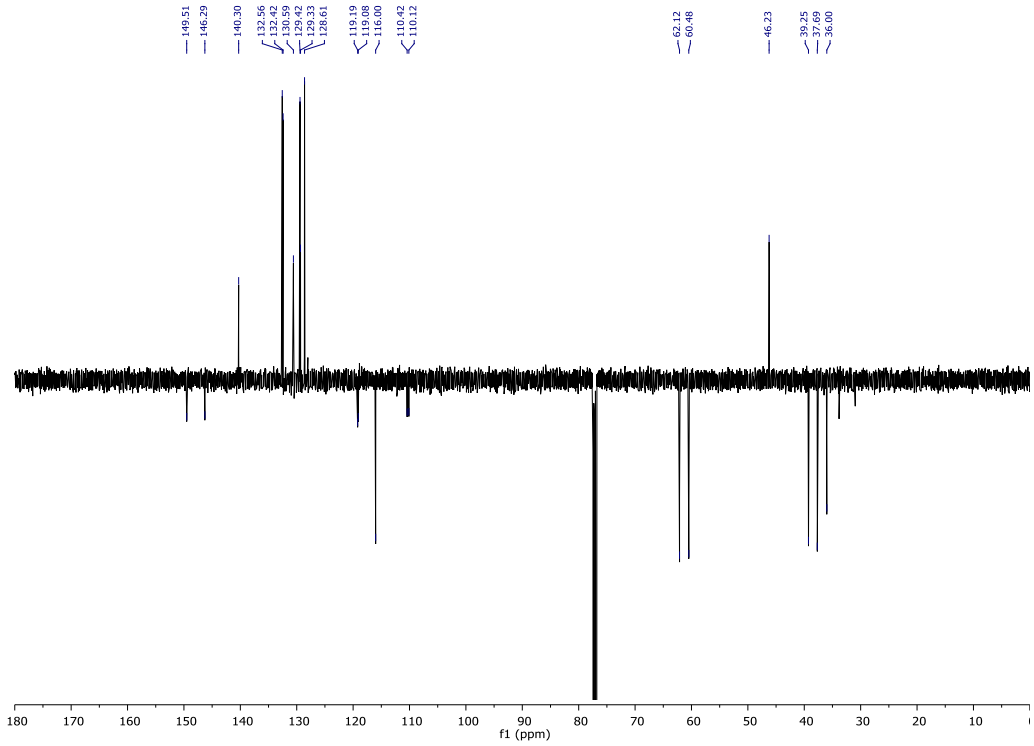


Fig. 3a, Compound **23**

(500 MHz, $CDCl_3$)



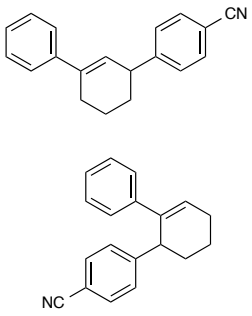
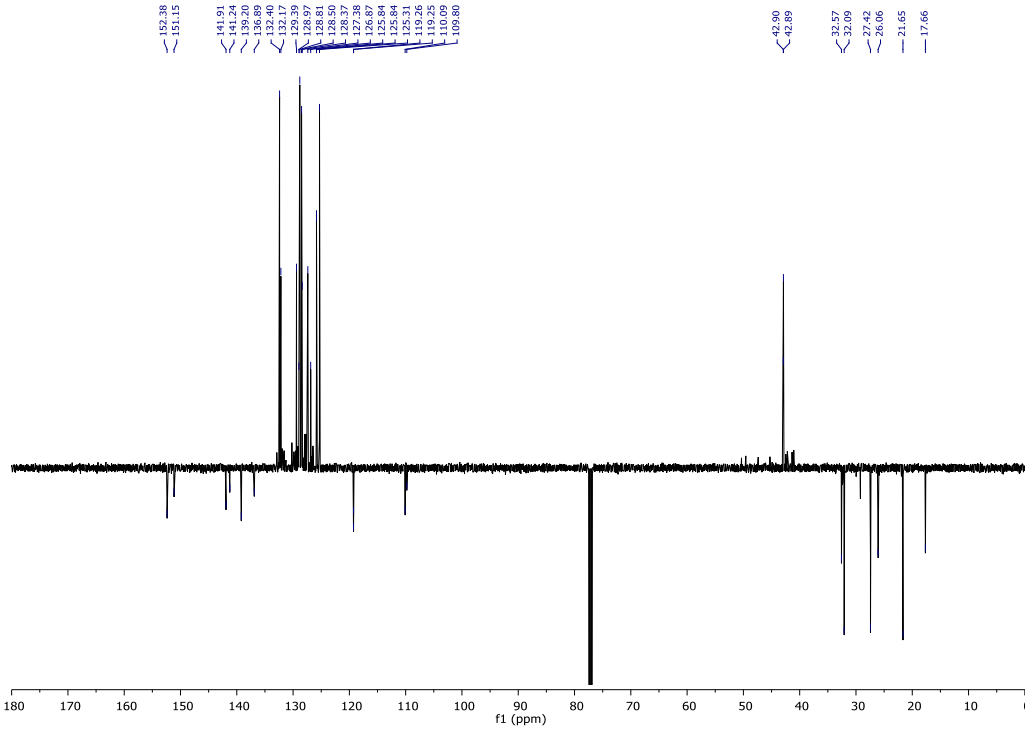


Fig. 3a, Compound **24**

(500 MHz, $CDCl_3$)



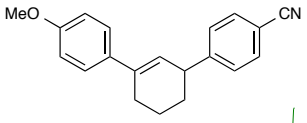
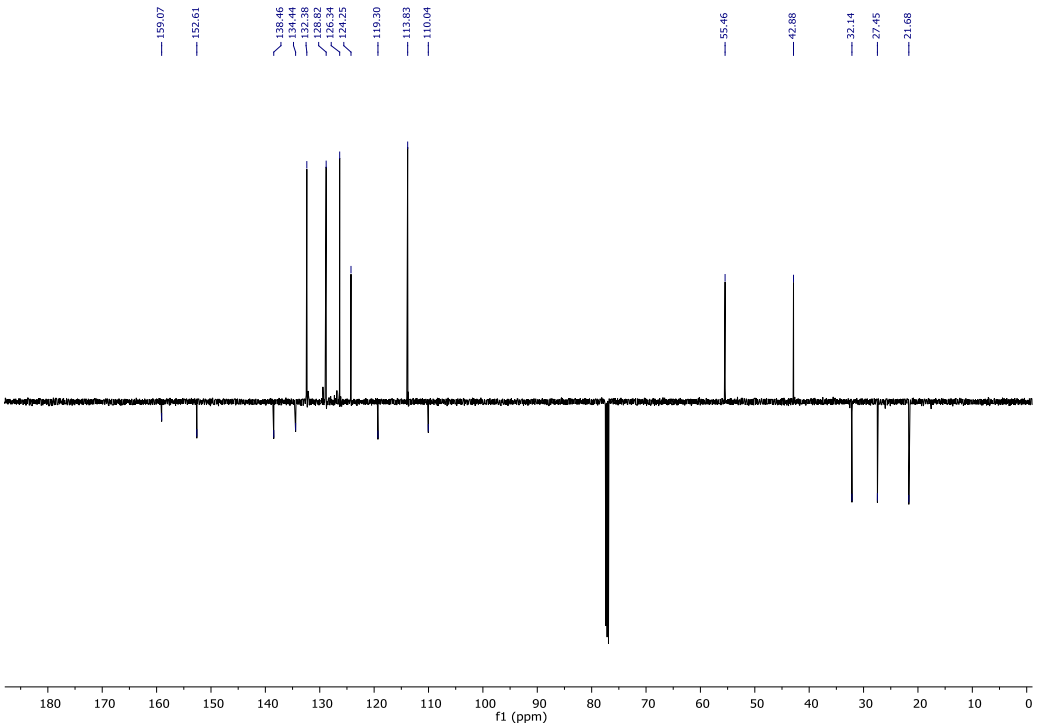


Fig. 3a, Compound **25**

(500 MHz, $CDCl_3$)



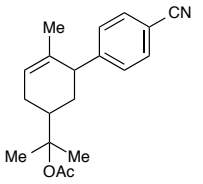
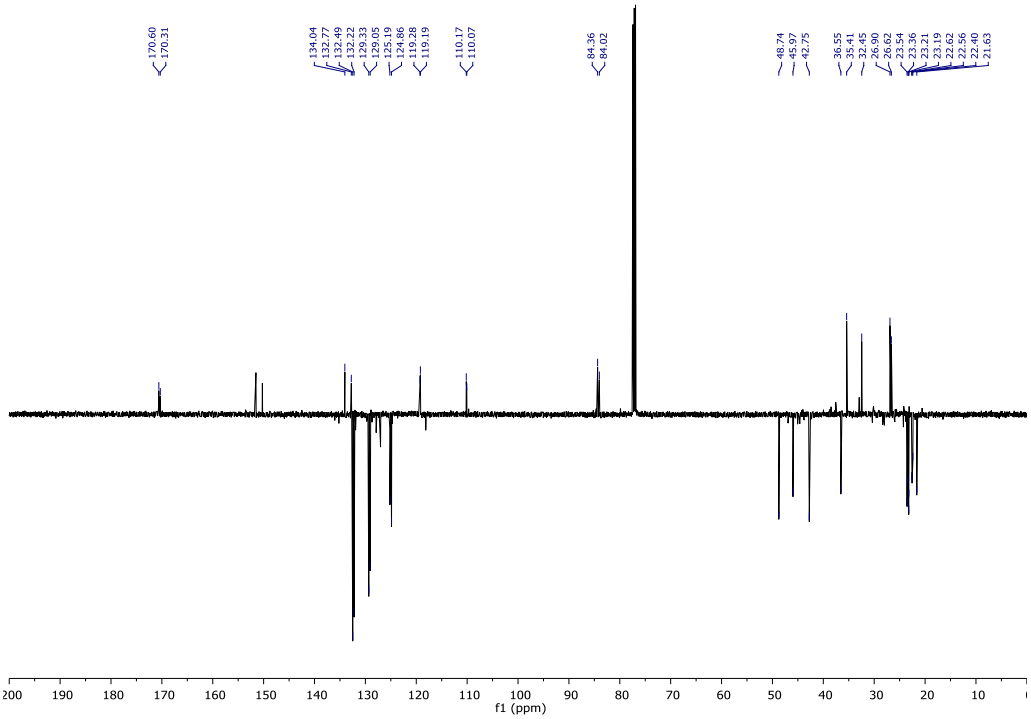


Fig. 3a, Compound **26**

(500 MHz, $CDCl_3$)



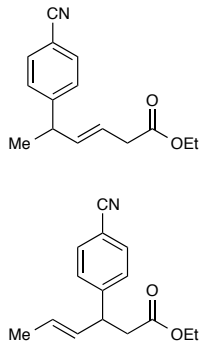
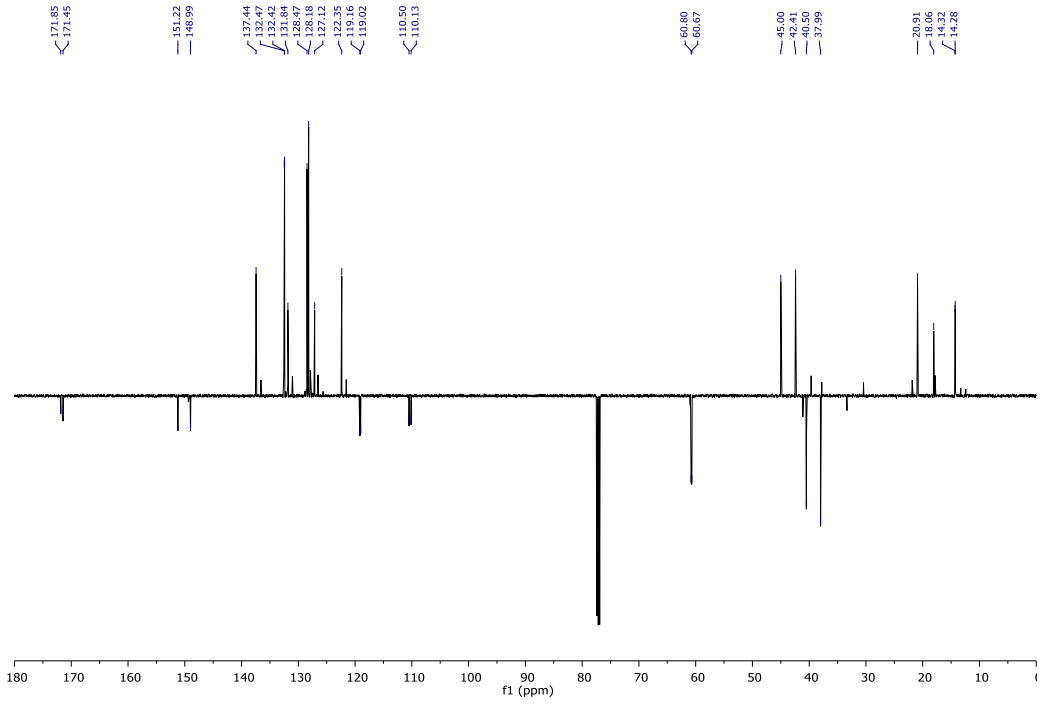


Fig. 3a, Compound **28**

(500 MHz, $CDCl_3$)



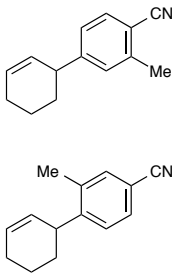
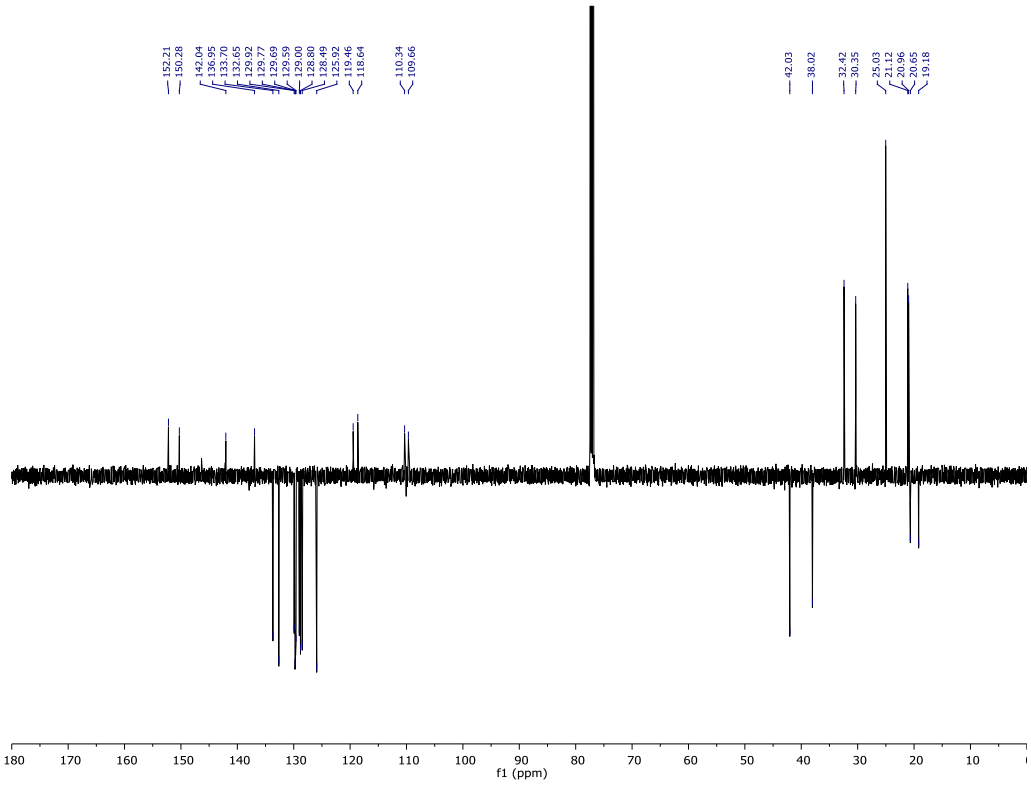


Fig. 3b, Compound **29**

(500 MHz, $CDCl_3$)



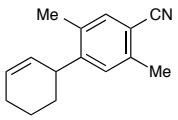
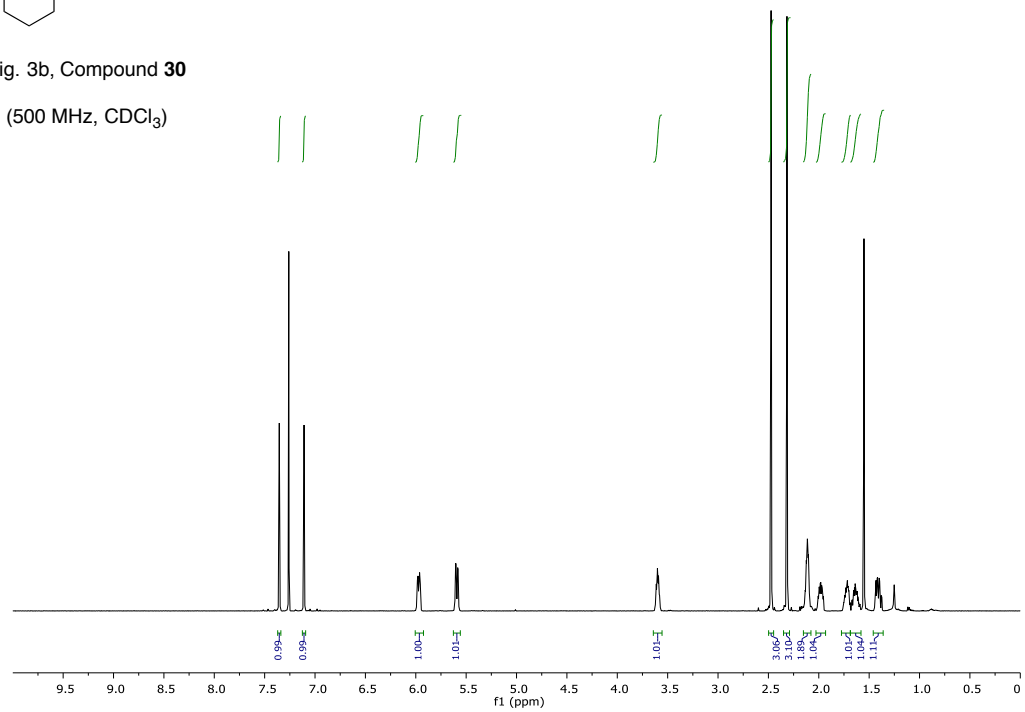
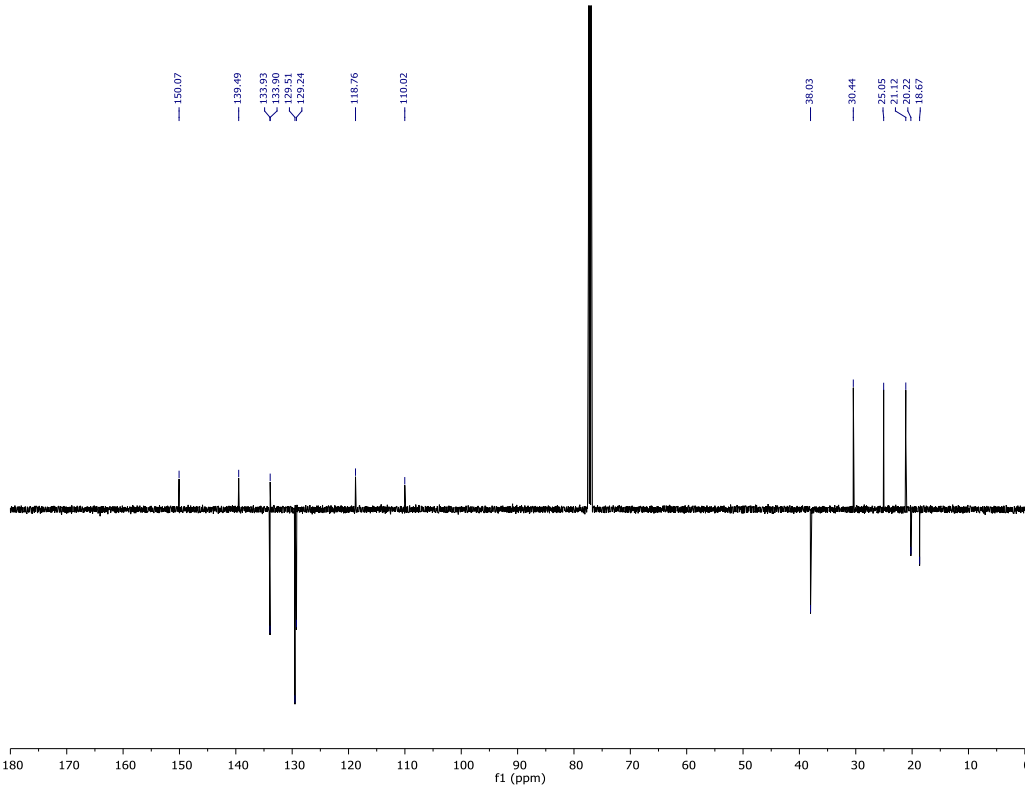


Fig. 3b, Compound **30**

(500 MHz, $CDCl_3$)





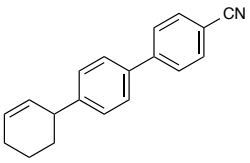
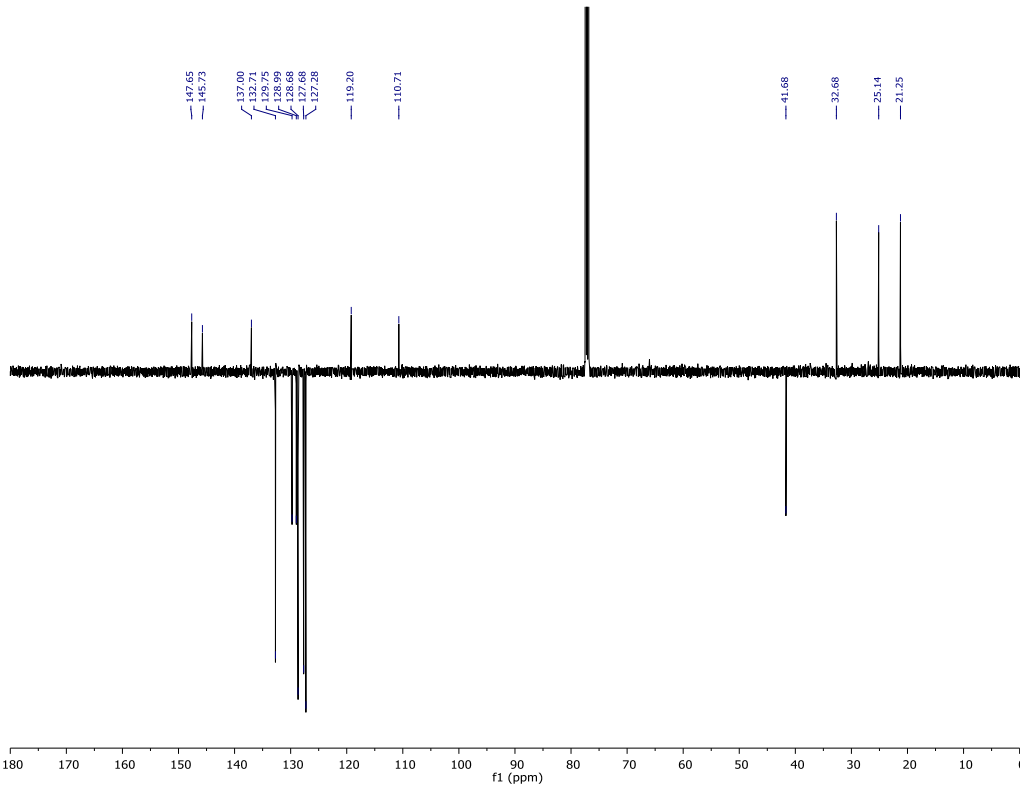


Fig. 3b, Compound **32**

(500 MHz, $CDCl_3$)



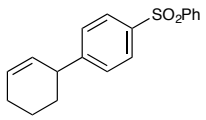
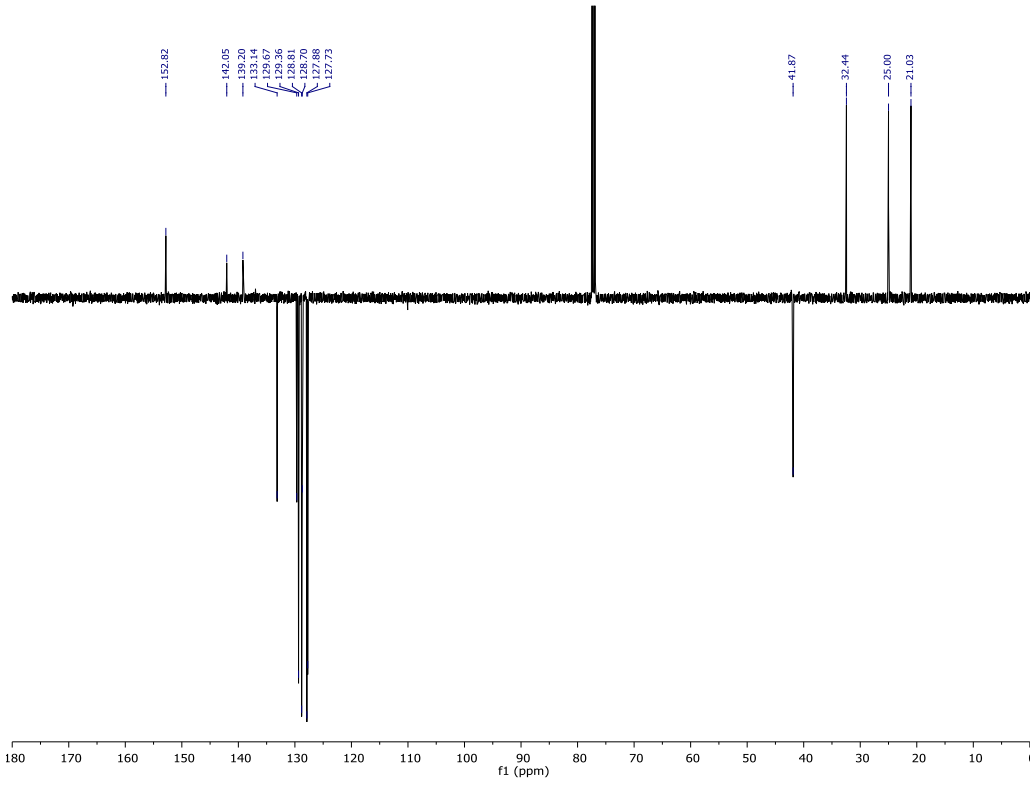


Fig. 3b, Compound **33**

(500 MHz, $CDCl_3$)



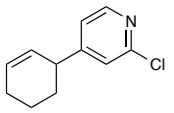
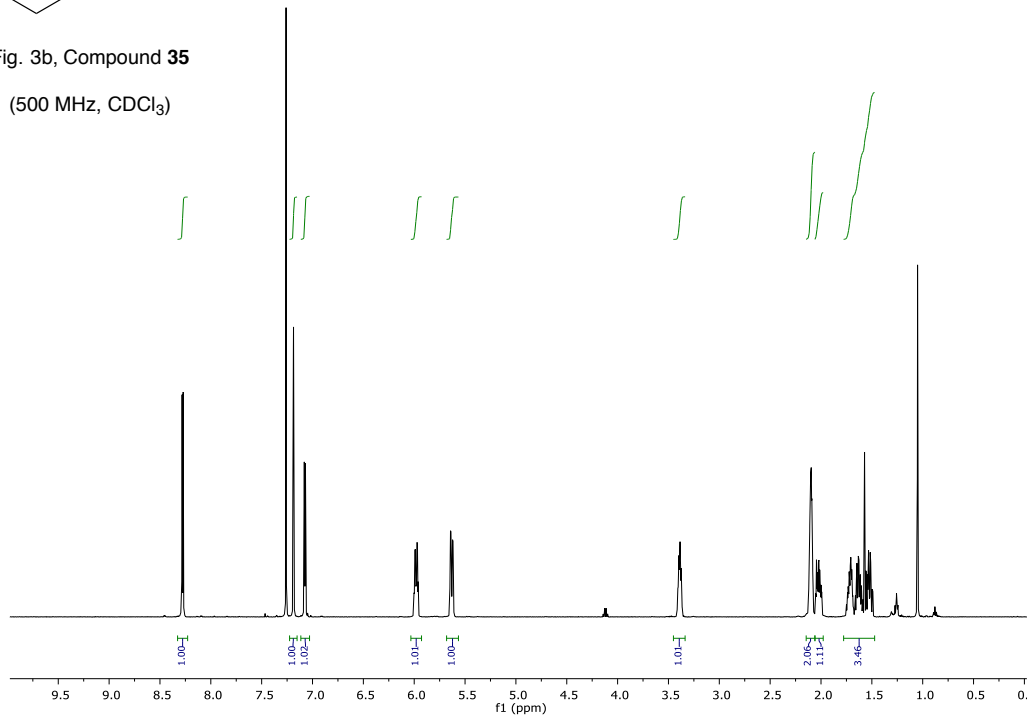
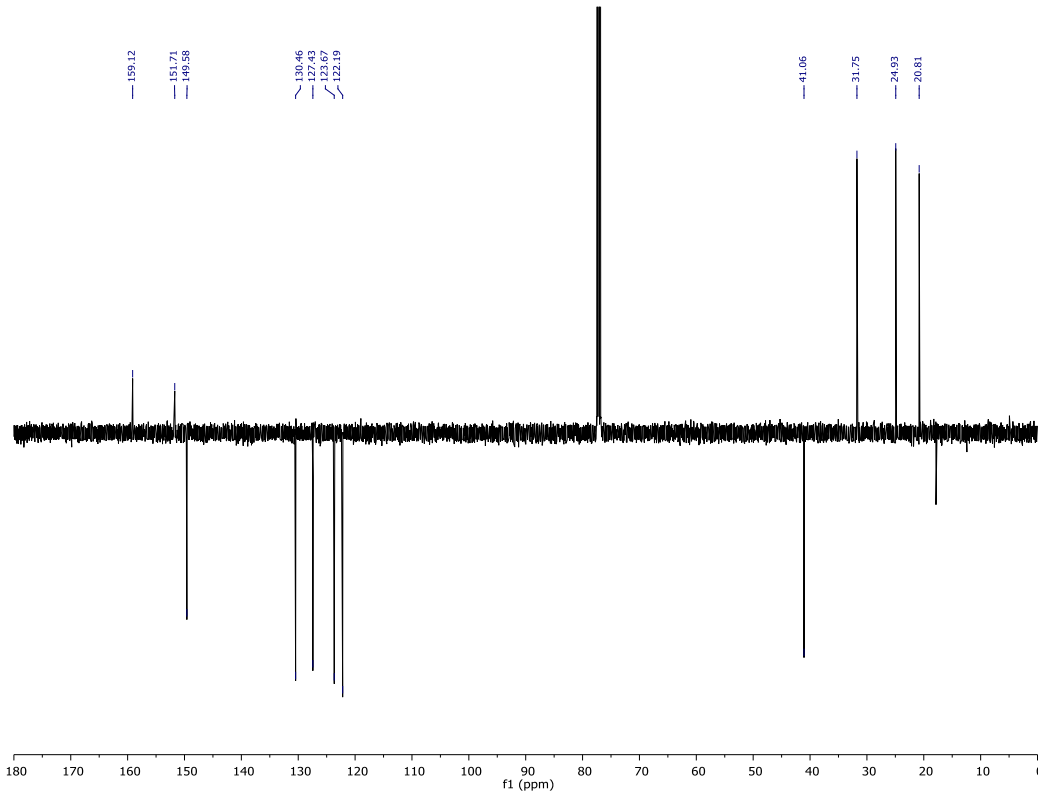


Fig. 3b, Compound **35**

(500 MHz, $CDCl_3$)





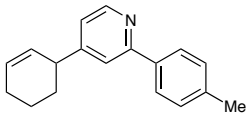
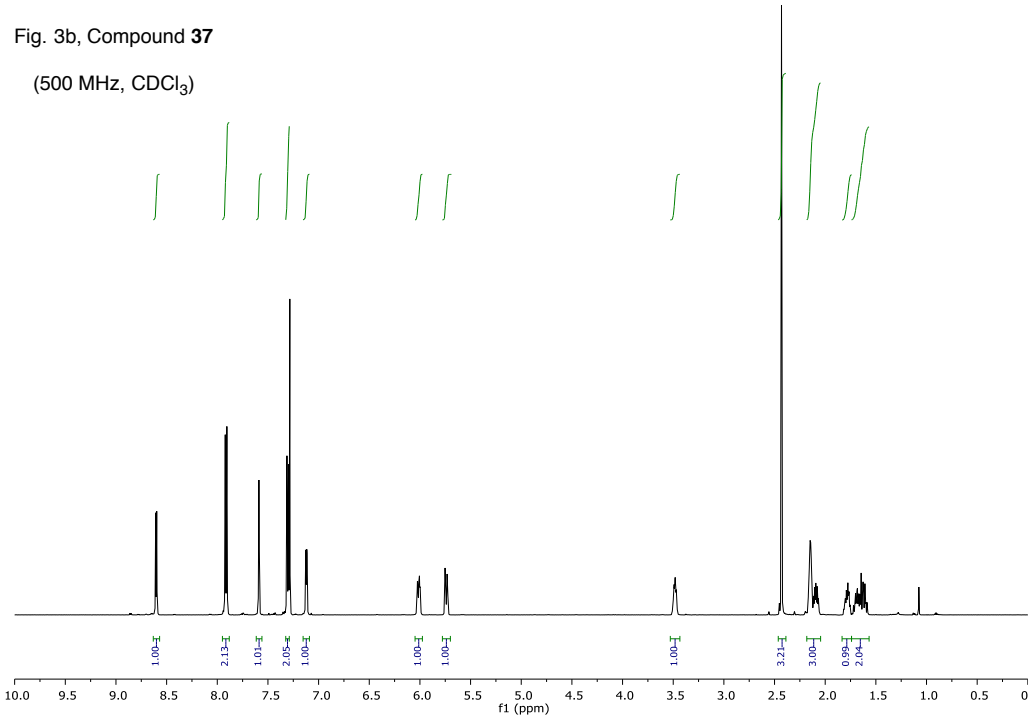
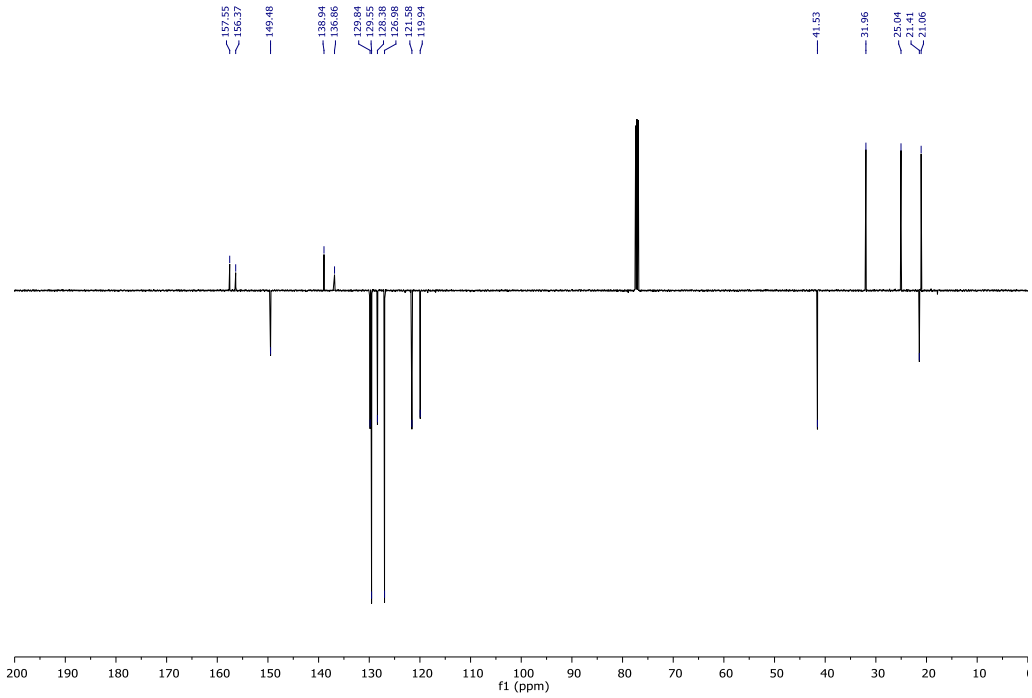


Fig. 3b, Compound **37**

(500 MHz, $CDCl_3$)





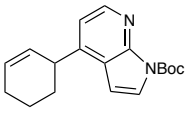
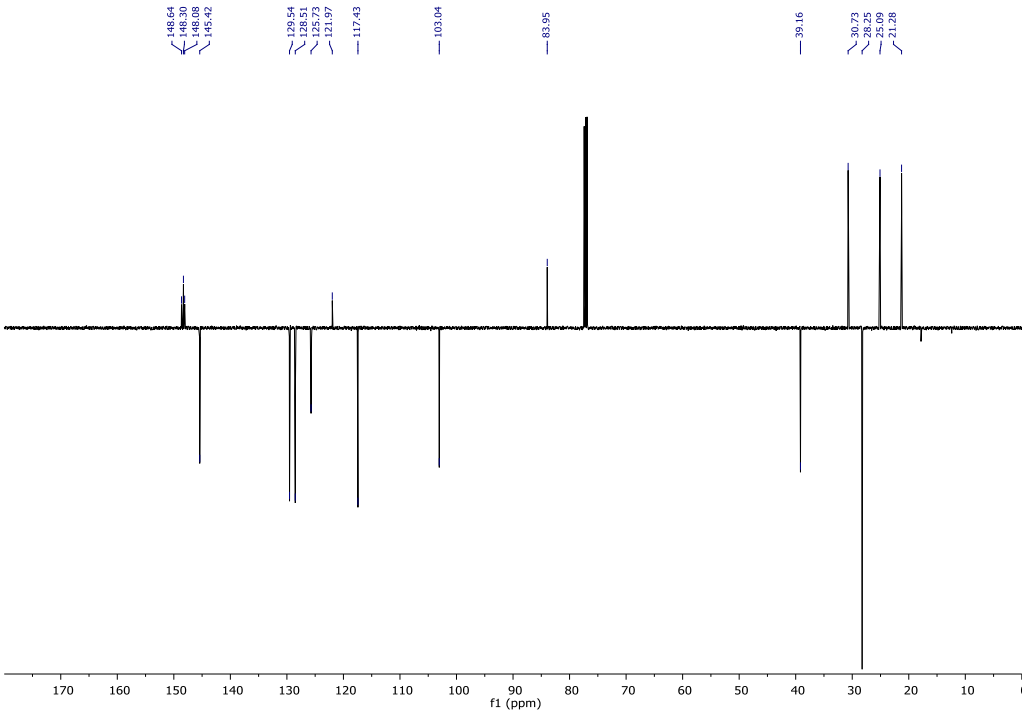


Fig. 3b, Compound **38**

(500 MHz, $CDCl_3$)



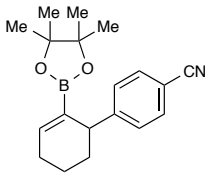
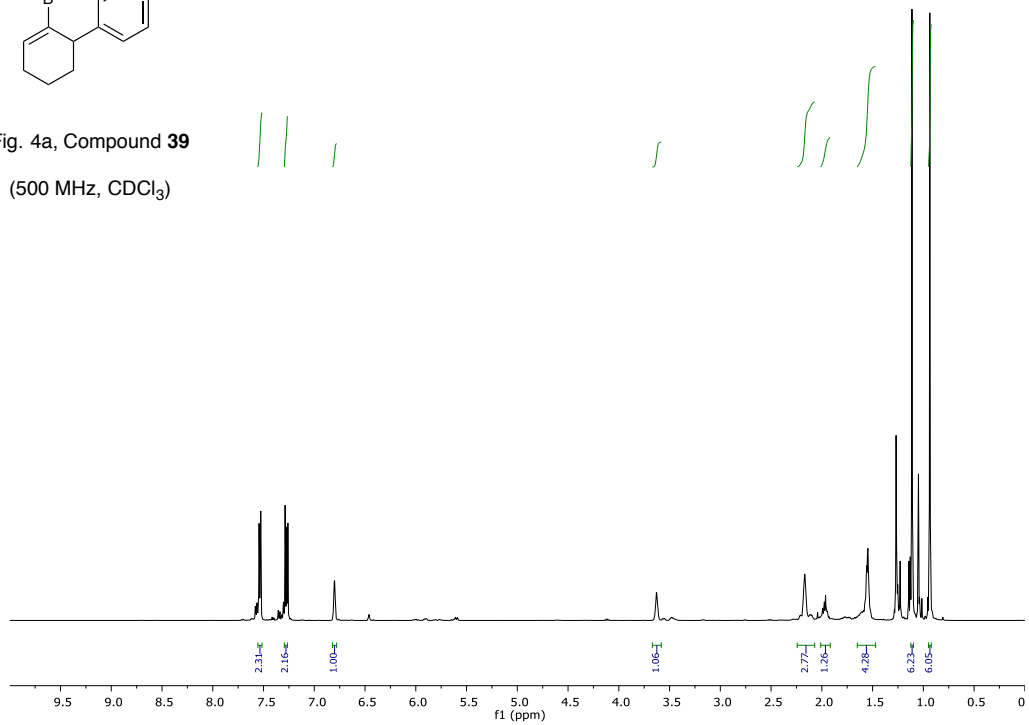
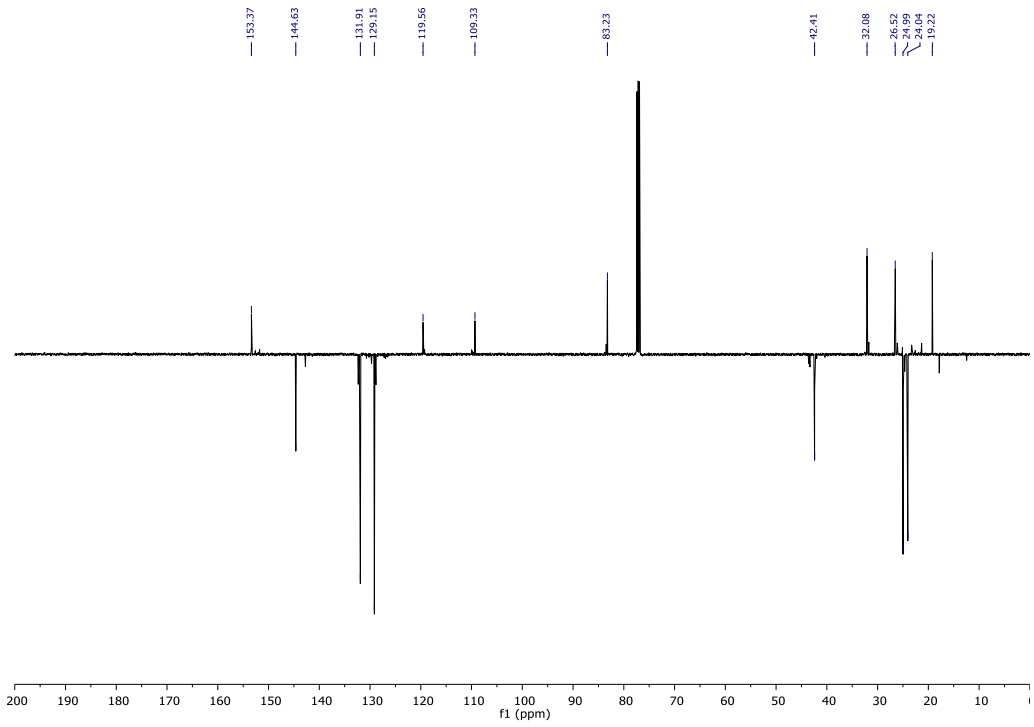


Fig. 4a, Compound **39**

(500 MHz, $CDCl_3$)





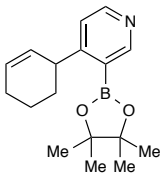
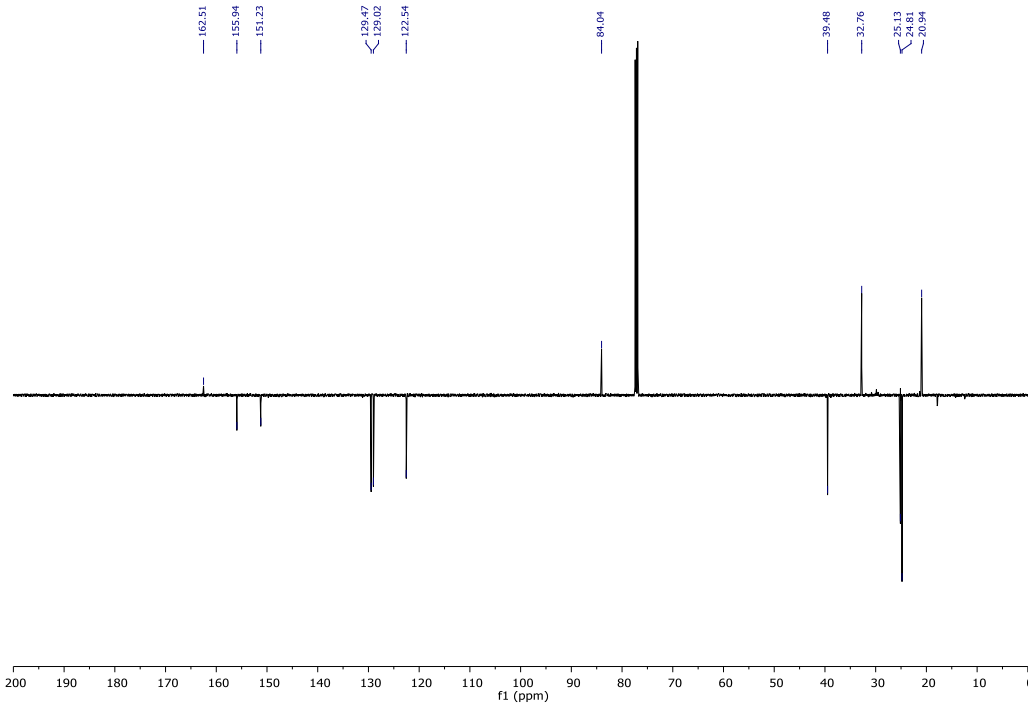


Fig. 4a, Compound **40**

(500 MHz, $CDCl_3$)



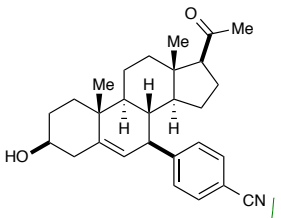
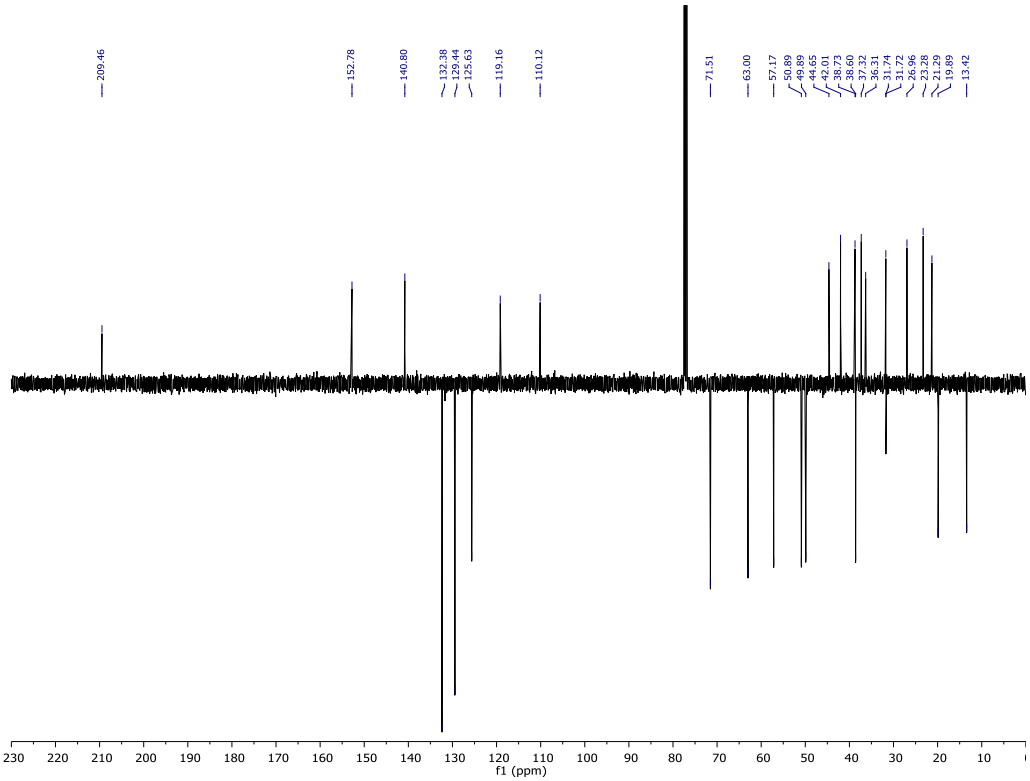


Fig. 4b, Compound **41**

(500 MHz, $CDCl_3$)



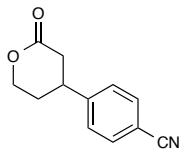


Fig. 4c

(500 MHz, $CDCl_3$)